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AMERICAN CHEMICAL JOURNAL.

ON THE REVERSION OF PHOSPHORIC ACID.

BY THOMAS S. GLADDING.

In a previous paper¹ the writer has demonstrated, among minor considerations, the following points :

I. That reverted phosphoric acid exists in three forms in commercial superphosphates :

- (a) as reverted phosphate of lime,
- (b) “ “ “ “ iron,
- (c) “ “ “ “ alumina.

II. That artificially precipitated phosphate of lime, whether the di-calcic or tri-calcic form, when mixed with sulphate of lime (as is the case in a superphosphate) and exposed to atmospheric conditions in shade in open vessels for several days and dried to a fine powder, is readily and completely soluble in a neutral solution of citrate of ammonia, at the temperature of 40° C.

III. That artificially precipitated phosphates of iron and alumina, when treated in the same way, become largely insoluble in the citrate of ammonia solution, at the temperature of 40° C.

IV. That a citrate of ammonia solution alone, of all the solvents that have been proposed, is a perfect solvent for all the forms of reverted phosphates (as they exist in superphosphates), while at the same time it does not unduly dissolve the crude or insoluble phosphate present.

¹ This Journal, 4, 123; and Chemical News, 46, 18, 31.

V. Lastly, and most important of all, the citrate of ammonia solution, in order to be a perfect solvent for reverted phosphates of iron and alumina, as they exist in commercial superphosphates, must be used at a temperature of 65° C. (150° F). At this temperature every form of reverted phosphate is dissolved.

In the present publication the above points are more fully sustained by additional experiments, and the investigation has been extended to a consideration of the reversion of soluble phosphates in artificial and natural soils.

The inquiry may be divided for the sake of clearness into the following heads:

- I. Experiments on natural phosphates,
- II. " " artificial soils,
- III. " " natural "

I.—EXPERIMENTS ON NATURAL PHOSPHATES.¹

To make the investigation on this point as conclusive as possible, a very large number of natural phosphates, embracing nearly every commercial article, was collected. These samples were all ground to pass through a 60 mesh sieve; no further grinding nor trituration being employed. Several liters of a neutral citrate of ammonia solution, specific gravity 1.09, were prepared. One gram of each phosphate was accurately weighed, and washed into a 200 cc. flask with 50 cc. of the above solution. The flask was corked and the contents digested for 30 minutes as follows:

- 1st. One gram with neutral solution at temp. of 40° C.
- 2d. " " " " " " " " 65° C.
- 3d. " " " ammoniacal " " " " "
- 4th. " " " stronger " " " " "
- 5th. " " " acid " " " "

In digestion 3d, $\frac{1}{2}$ cc. of 20 per cent. ammonia solution was added to every 50 cc. solution of citrate of ammonia.

In digestion 4th, 1 cc. of 20 per cent. ammonia solution was added to every 50 cc. of citrate of ammonia solution.

In digestion 5th, .753 gram of citric acid was added to every 50 cc. of citrate of ammonia solution. This quantity is just equivalent to .200 gram of ammonia, the amount of free ammonia added to every 50 cc. in digestion 4th.

¹ For many of the samples used thanks are due to Dr. C. U. Shepard, Jr.

Lime Phosphates.

No.	Commercial Name.	Digestion 1st. With neutral citrate of ammonia solution, temperature 40° C.	Digestion 2d. With neutral citrate of ammonia solution, temperature 65° C.	Digestion 3d. With neutral citrate of ammonia solution, with ½ cc. ammonia added to each 50 cc. temperature 65° C.	Digestion 4th. With neutral citrate of ammonia solution, with 1 cc. of ammonia added to each 50 cc. temperature 65° C.	Digestion 5th. With neutral citrate of ammonia solution, with .753 gram citric acid added to each 50 cc. temperature 65° C.
		Per cent. Phos. acid dis.	Per cent. Phos. acid dis.	Per cent. Phos. acid dis.	Per cent. Phos. acid dis.	Per cent. Phos. acid dis.
1.	Apatite (Canadian).....	.30	.56	.39
2.	Caceres (Spain).....	.41	.38	.47
3.	Cambridgeshire Cops.....	.56	.85	.44
4.	Logrosan.....	.68	.41	.66
5.	Oruba.....	1.22	2.09	1.14
6.	Curacao.....	1.28	1.35	.95
7.	Bedfordshire Cops.....	1.38	1.18	.95
8.	Fr. Ph'rite, Dept. Lot.....	1.64	1.88	1.50
9.	Fr. Ph'rite, Lot-et-Gar.....	1.88	1.90	1.59
10.	Sombrero.....	1.84	2.29	2.00
11.	Avalo (fine).....	1.96	2.12	1.82
12.	Orchilla.....	4.63	4.81	3.67
13.	Bone Black.....	5.47	6.13	4.00
14.	Avalo (lump).....	5.60	5.83	4.48
15.	Raza Island (Gulf Cal.).....	5.92	6.17	5.71
16.	Lahn Phosphorite.....	.82	.76	1.35	...	1.59
17.	Suffolk Cops.....	2.83	2.73	2.05	...	5.00
18.	Bone Ash.....	2.97	3.93	2.61	...	5.71
19.	Mona Island.....	6.47	6.82	5.91	...	9.31
20.	Per. Guano (Tarapaca).....	12.74	13.14	11.99	8.98	16.17
21.	So. Carolina (river).....	1.09	1.35	1.06	1.06	2.89
22.	Navassa.....	2.73	2.53	1.86	1.22	4.87
23.	Curacao Guano.....	6.00	6.19	4.59	3.86
Average (No. 1).....		2.91	3.17	2.76
Average (No. 2)..... (20 to 23 inclusive.)		...	5.80	4.85	3.78	...
Average (No. 3)..... (16 to 22 inclusive.)		...	4.46	6.50

Iron and Alumina Phosphates.

No.	Commercial Name.	Per cent. Phos. acid dis.	Per cent. Phos. acid dis.	Per cent. Phos. acid dis.	Per cent. Phos. acid dis.	Per cent. Phos. acid dis.
24.	Grand Connetable.....	1.16	1.97	5.82	11.44	1.12
25.	El Roque.....	1.36	1.96	4.27	5.68	...
Average (No. 4).....		1.26	1.96	5.04	8.56	1.12

Besides the general interest which attaches to the above table, as showing the relative solubility of the different natural phosphates when treated exactly alike with citrate of ammonia solution, the following points are worthy of consideration :

1. A slight acidity of the solution largely increases the quantity of raw phosphate dissolved, as is shown by average (3).

2. A slight alkalinity decreases, to a marked extent, the solvent action on all phosphates of lime, as is shown by averages (1) and (2).

3. A stronger alkalinity decreases still more this solvent action on phosphates of lime, as is shown by average (2).

4. An alkalinity increases, on the other hand, the solvent power of the citrate of ammonia solution on phosphates, when the phosphoric acid exists as phosphates of iron and alumina, and not as phosphate of lime, as is shown by average (4).

As the aim of the ideal method of determining reverted phosphoric acid is to separate the precipitated phosphates from the original insoluble phosphate still left in a fertilizer, it follows from the above four points that the *neutral* citrate of ammonia solution is decidedly superior to either an acid or ammoniacal solution.

5. A change in the temperature of digestion, from 40° C. to 65° C., increases only slightly the solvent action on natural phosphates, as is shown by average (1) ; the increase being from 2.91 per cent. to 3.17 per cent. ; a difference of only 0.26 per cent.

II.—EXPERIMENTS ON ARTIFICIAL SOILS.

In these experiments, finely ground sand was used to represent the soil mass.

With weighed and separate portions of this were mixed weighed quantities of

- (1) Carbonate of lime (freshly precipitated),
- (2) Oxide of iron (freshly precipitated),
- (3) Oxide of aluminum (freshly precipitated),
- (4) Brown¹ hematite (finely ground),
- (5) Bauxite² (finely ground).

Experiment No. 1.

(a) To a mixture of 5 grams fine sand with 0.250 gram of carbonate of lime, was added .200 gram sodium ammonium phos-

¹ Brown hematite comp. $H_6Fe_2O_9$ = sesquioxide iron 85.6 per cent., water 14.4 per cent.

² Bauxite comp. perhaps $Al(Fe)O_3 + 2Aq.$ Dana.

phate dissolved in water. After exposure in an open vessel and drying in the shade, for 72 hours, in this manner, it was divided into two equal parts and digested in neutral ammonium citrate solution 30 minutes with the following results:

Temperature 40° C., phosphoric acid dissolved .0767 gram ; temperature 65° C., phosphoric acid dissolved .0761 gram ; showing that the reverted phosphate was completely dissolved at both temperatures.

(b) Mixture of 5 grams fine sand ; .500 gram precipitated carbonate of lime with solution of .500 gram sodium ammonium phosphate was exposed in an open vessel, *in the sun*, 72 hours. After drying in this manner it was digested with citrate of ammonia solution at temperature 40° C., and all the reverted phosphoric acid was dissolved.

(c) A similar mixture, treated in the same manner, except that it was exposed in the shade, gave the same results.

Experiment No. 2.

Conducted in the same manner as Experiment No. 1 (a). Mixture 5 grams fine sand, 1 gram freshly precipitated sesquioxide of iron, solution .500 gram sodium ammonium phosphate, containing about .190 gram phosphoric acid. (There was no lime present.)

One-half digested with citrate of ammonia, temperature 40° C., phosphoric acid added and afterwards reverted = .095 gram ; reverted phosphoric acid dissolved = .0653 gram.

One-half digested with citrate of ammonia, temperature 65° C., phosphoric acid added and afterwards reverted = .095 gram ; reverted phosphoric acid dissolved = .096 gram.

Amount of reverted phosphoric acid not dissolved at 40° C. .0297 gram.

The mixture was tested for soluble and only a trace found.

Experiment No. 3.

Conducted in the same manner as Nos. 1 and 2. Mixture 5 grams fine sand, 1 gram freshly precipitated hydrate of alumina, with solution of .500 gram sodium ammonium phosphate, containing about .190 gram phosphoric acid.

After 72 hours, one-half digested with citrate ammonia, temperature 40° C., phosphoric acid added = .095 gram, reverted phosphoric acid dissolved = .0535 gram. One-half digested with citrate

of ammonia, temperature 65° C., phosphoric acid added = .095 gram, reverted phosphoric acid dissolved = .0943 gram; amount of reverted phosphoric acid not dissolved at 40° C. .0415 gram. The mixture was tested for soluble *and only a trace found*.

Experiment No. 4.

Conducted in the same manner as Experiments 1, 2 and 3. Mixture 30 grams fine sand, 3 grams brown hematite, with solution of .750 gram sodium ammonium phosphate, containing about .261 gram phosphoric acid.

After 72 hours, divided into three equal parts, one-third digested with citrate of ammonia, temperature 40° C., phosphoric acid present = .091 gram, phosphoric acid dissolved = .076 gram, reverted phosphoric acid dissolved = .0503 gram. One-third digested with citrate of ammonia, temperature 65° C., phosphoric acid present = .091 gram, phosphoric acid dissolved = .089 gram, reverted phosphoric acid dissolved = .0633 gram. One-third digested with cold water, phosphoric acid present = .091 gram, phosphoric acid dissolved = .0257 gram, reverted phosphoric acid dissolved = .0653 gram.

Total reverted phosphoric acid present = .0653 gram; amount total reverted phosphoric acid present not dissolved at 40° C., .015 gram.

Experiment No. 5.

Conducted in same manner as Experiments 1, 2, 3 and 4. Mixture 30 grams fine sand, 3 grams bauxite, with solution of .750 gram sodium ammonium phosphate, containing about .261 gram phosphoric acid.

After 72 hours, divided into three equal parts, one-third digested with citrate of ammonia, temperature 40° C., phosphoric acid present = .091 gram, phosphoric acid dissolved = .080 gram, reverted phosphoric acid dissolved = .0457 gram. One-third digested with citrate of ammonia, temperature 65° C., phosphoric acid present = .091 gram, phosphoric acid dissolved = .0915 gram, reverted phosphoric acid dissolved = .0571 gram. One-third digested with cold water, phosphoric acid present = .091 gram, phosphoric acid dissolved = .0344 gram, reverted phosphoric acid dissolved = .0566 gram.

Total reverted phosphoric acid present = .0566 gram; amount total reverted phosphoric acid present not dissolved at 40° C., .0109 gram.

Experiment No. 1 (*a, b, c*) shows that ammonium citrate solution at 40° C. dissolved all the reverted phosphates of lime.

Experiment No. 2 shows that at temperature of 65° C. ammonium citrate solution dissolved all the reverted phosphate of iron present, while at temperature of 40° C. it failed to dissolve 31.26 per cent. of the phosphoric acid actually reverted.

Experiment No. 3 shows that at temperature of 65° C. ammonium citrate solution dissolved all the reverted phosphates of alumina present, while at temperature of 40° C. it failed to dissolve 43.68 per cent. of the phosphoric acid actually reverted.

Experiment No. 4 shows that at temperature of 65° C. ammonium citrate solution dissolved all the reverted phosphate present, while at temperature of 40° C. it failed to dissolve 22.68 per cent. of the phosphoric acid actually reverted.

Experiment No. 5 shows that at temperature of 65° C. ammonium citrate solution dissolved all the reverted phosphate present, while at temperature of 40° C. it failed to dissolve 17.49 per cent. of the phosphoric acid actually reverted.

III.—EXPERIMENTS ON NATURAL SOILS.

The soils used were light loams; one from the truck gardens of Long Island, N. Y., one from the cotton plantations of North Carolina, and one from the tobacco fields of Connecticut; taken from plots upon which fertilizers have been sown and large crops of the above staples grown.

The soils were ground to pass through a 20 mesh sieve, and 100 grams of each were weighed for each experiment.

160 grams of an ammoniated superphosphate were digested in 2 liters of water and filtered; the quantity of phosphoric acid found by analysis in 50 cc. of this filtrate was .284 gram. This quantity was added to 100 grams of each soil as prepared above, and the mixture was stirred to a thin, wet, pasty condition; allowed to remain five days in thin layer, exposed to the open atmospheric conditions, in the shade, in open vessels; at the end of this period they were weighed and divided into four equal parts for digestion in citrate of ammonia solution, at temps. 40° C. and 65° C., and with water, to determine amount not reverted.

In order to calculate the exact quantity of reverted dissolved by these digestions, the amount originally in each soil was estimated by previous digestions as follows:

Soil.	Amount Phosphoric Acid dissolved from 25 grams by Citrate of Ammonia, tem- perature 40° C.	Amount Phosphoric Acid dissolved from 25 grams by Citrate of Ammonia, tem- perature 65° C.	Amount Phosphoric Acid dissolved from 25 grams by water.
No. 1. Long Island garden,	.0193 gram	.0292 gram	trace
2. North Carolina cotton,	.003	.0076	"
3. Connecticut tobacco,	.0072	.0163	"

Corrections have been made, according to the above results, in the following tables:

Soil Experiment No. 1.—Long Island Garden Soil.

25 gram mixture, digested with citrate of ammonia, temperature 40° C., phosphoric acid added = .071 gram ; phosphoric acid dissolved = .0532 gram ; reverted phosphoric acid dissolved = .0462 gram.

25 gram mixture, digested with citrate of ammonia, temperature 65° C., phosphoric acid added = .071 gram ; phosphoric acid dissolved = .0702 gram ; reverted phosphoric acid dissolved = .0632 gram.

25 gram mixture, digested with water, phosphoric acid added = .071 gram ; phosphoric acid dissolved = .007 gram ; reverted phosphoric acid dissolved = .064 gram.

Amount of phosphoric acid added, actually reverted = .064 gram ; amount phosphoric acid added, actually reverted and not dissolved at 40° C. = .0178 gram.

Soil Experiment No. 2.—North Carolina Cotton Soil.

25 gram mixture, digested with citrate of ammonia, temperature 40° C., phosphoric acid added = .071 gram ; phosphoric acid dissolved = .053 gram ; reverted phosphoric acid dissolved = .0468 gram.

25 gram mixture, digested with citrate of ammonia, temperature 65° C., phosphoric acid added = .071 gram ; phosphoric acid dissolved = .0713 gram ; reverted phosphoric acid dissolved = .0651 gram.

25 gram mixture, digested with water, phosphoric acid added = .071 gram ; phosphoric acid dissolved = .0062 gram ; reverted phosphoric acid dissolved = .0648 gram.

Amount of phosphoric acid added, actually reverted = .0648 gram ; amount of phosphoric acid added, actually reverted and not dissolved at 40° C. = .018 gram.

Soil Experiment No. 3.—Connecticut Tobacco Soil.

25 gram mixture, digested with citrate of ammonia, temperature 40° C., phosphoric acid added = .071 gram; phosphoric acid dissolved = .052 gram; reverted phosphoric acid dissolved = .046 gram.

25 gram mixture, digested with citrate of ammonia, temperature 65° C., phosphoric acid added = .071 gram; phosphoric acid dissolved = .0698 gram; reverted phosphoric acid dissolved = .0638 gram.

25 gram mixture, digested with water, phosphoric acid added = .071 gram; phosphoric acid dissolved = .006 gram; reverted phosphoric acid dissolved = .065 gram.

Amount of phosphoric acid added, actually reverted = .065 gram; amount of phosphoric acid added, actually reverted and not dissolved at 40° C. = .019 gram.

Experiment No. 1 shows that citrate of ammonia solution at temperature of 65° C. dissolves all the phosphoric acid added to the soil, while at temperature 40° C. it fails to dissolve 27.81 per cent. of the phosphoric acid actually reverted by the soil.

Experiment No. 2 shows that citrate of ammonia solution at temperature of 65° C. dissolves all the phosphoric acid added to the soil, while at temperature of 40° C. it fails to dissolve 27.77 per cent. of the phosphoric acid actually reverted by the soil.

Experiment No. 3 shows that citrate of ammonia solution at temperature 65° C. dissolves all the phosphoric acid added to the soil, while at temperature of 40° C. it fails to dissolve 29.23 per cent. of the phosphoric acid actually reverted by the soil.

In order to obtain a thorough and uniform mixture of the solution of phosphoric acid with so large a volume of soil, the mass was made very wet and stirred. During two days its condition represented very wet lands; later, as more water evaporated, it took upon itself all the successive stages of drouth, but at no time contained less moisture than was observed in the fields from the surface to depths varying several inches during the summer season. Tests made with other portions of these mixtures showed that all the phosphoric acid was dissolved at both temperatures, if kept constantly saturated with water, owing to the ready solubility of all gelatinous precipitates at low temperatures.

Whether phosphoric acid exists in the soil in combination with lime only, or also with iron and alumina, has heretofore never

been proven by any direct laboratory tests, because no method of separation was known for distinguishing these three phosphates in the presence of each other in the soil. The results of soil experiments 1, 2, 3 (pp. 4, 5) show that advantage can be taken of this discovery to formulate a method of a laboratory qualitative test for reverted iron and alumina phosphates, under the above conditions. The fact that a strongly alkaline citrate of ammonia solution rapidly attacks insoluble iron and alumina phosphates, but dissolves even less of insoluble lime phosphate than when neutral, constitutes another test for distinguishing these phosphates.

Many investigators have sought a direct proof since the work of Thénard¹ on this subject, but I am not aware that any has been found.

That phosphoric acid becomes reverted, or insoluble in water, when in contact with soil, has been demonstrated by many experiments by such noted scientists as Bronner,² Thompson and Huxtable,³ Way,⁴ Liebig,⁵ Mulder,⁶ Knop and Hussakowsky,⁷ Salomon,⁸ Millot,⁹ Joullie,¹⁰ Voelcker,¹¹ and in our own country by Drs. Johnson¹² and Shepard.¹³

Of these, a large number believed that it becomes combined largely with iron and alumina. Knop especially proved that phosphoric acid was fixed in greater amount, and more rapidly, when oxides of these bases were *added* to soils, and that soils containing *large quantities* had greater reverting properties than those containing *less* oxides of iron and alumina.

Thénard and Déhérain discussed elaborate theories to establish the chemical reaction by which plants could absorb phosphoric acid from its combinations with iron and alumina; but experience has taught the agriculturist that he cannot reason with certainty regarding these intricate processes.

That plants do absorb phosphoric acid from pure phosphate of iron and alumina, by *some means*, has been demonstrated beyond a doubt in recent field experiments by Drs. Peterson,¹⁴ Voelcker,¹⁵

¹ Comptes Rendus, 1856, 46, 212.

² Treatise 1836, and Jahresbericht der ag. Chemie, 1863-64, 6.

³ Roy. Ag. Soc. Jour. Eng.

⁴ *Ibid.* 1850, 11, 313; 15, 91.

⁵ Annalen der Chemie und Physik, 105, 106.

⁶ Chemie der Akerkrume, 1, 465.

⁷ Knop's Agric. Chemie.

⁸ *Ibid.* 2, 177.

⁹ Annales Agronomique, 1880; Barrel, Jour. d'Agric. 1879. ¹⁰ Comptes Rendus, 1879, 1324.

¹¹ Roy. Ag. Soc. Jour. Eng. 1862, and 1, 1, p. 37.

¹³ Rural Carolinian, June, 1872.

¹² How Crops Feed; and Rpts. Conn. Ag. Soc.

¹⁴ Fühling's Landwirthschaft. Zeitung, 1876, 5, 336.

¹⁵ Royal Ag. Soc. Jour. 31, 1880, 152; 33, 1881, and 34, 1882.

Fittbogan,¹ Prof. Dietrich,¹ F. Oldenberg,¹ Renow,¹ and Dr. Birner,¹ Prof. Maercker,² Hoffmeister,³ and others.

Leaving the theoretical discussion of this question, the practical view of the case is best expressed in the following words from Prof. S. W. Johnson's work, "How Crops Feed" (p. 374): "The great beneficent law regulating these absorptions appears to admit of the following expressions: those bodies which are most rare and precious to the growing plant are by the soil converted into and retained in a condition not of absolute, but of relative insolubility, and are kept available to the plant by the continual circulation in the soil of the more abundant saline matters."

The quantities of iron and aluminum oxides introduced into the mixtures of artificial soils, with which Experiments 2, 3, 4, 5 (pp. 5, 6) were performed, were chosen according to the average amount of these oxides in soils.

Analyses of 87 soils, collected from all the farming districts of New York State by Emmons⁴ in 1846, show the average contents of iron oxide and alumina to be 7.79 per cent.; of lime, 0.84 per cent.

The average of 20 representative soils, collected in New Jersey by Cook,⁵ shows by analysis, oxide of iron and alumina 19.33 per cent.; lime 0.77 per cent.

And even in Ohio, where the geological formation is lime rock, the soils contain much more of these oxides than of lime. The average of 13 representative soils shows by analysis,⁶ oxide of iron and alumina 3 per cent.; lime 1.25 per cent.

Very many soils contain less than 0.15 per cent. of lime. The normal amount, it is safe to say, does not exceed 0.45 per cent. Lime is rapidly removed from soils by percolating waters. In formations of lime rock, huge caverns are formed by this process; whereas the iron and alumina of the rocks remain in the soils formed from them, with a consequent increase of the relative proportions between these bases and lime.

Knop,⁷ Salomon⁸ and others have shown that this loss of lime is also largely due to reactions in the soil, by which soluble compounds of lime are formed with nitric, sulphuric, muriatic and humic acids.

¹ Biedermann's Centralblatt, March, 1881, 156.

³ *Ibid.* Dec. 1881, 813.

⁵ *Ibid.* New Jersey, 1869.

⁷ Knop's Ag. Chemie, 2, 177.

² *Ibid.* June, 1881, 378.

⁴ Geol. Report New York State, 1846.

⁶ *Ibid.* Ohio, 1870.

⁸ *Ibid.*

Albert and Vollbrecht¹ experimented on soils containing a large amount of lime, and with others containing a small amount, with the results here given in abstract :

They mixed 10 grams soil, containing 18.1 per cent. carbonate of lime ; 2.5 grams superphosphate, containing 9.3 per cent. phosphoric acid, soluble in water, and 12.06 per cent. reverted, soluble at temperature 40° C. in neutral solution of citrate of ammonia. Of the total phosphoric acid present,

In the shade, there became insoluble in water,	After hours.			Days.				
	4	8	12	3	6	8	10	14
	Per cent.			Per cent.				
	78	88.4	90.2	91.1	91.7	93.4	93.8	95

There became insoluble in citrate of ammonia

at temperature 40° C.,	2.1	3	4.1	4.1	4.1
In the sun, there became insoluble in water,	97.4	...	100
In citrate of ammonia at 40° C.,	4.6	...	6.6

Soil containing small amount of lime mixed with the same superphosphate ; of total phosphoric acid present,

There became insoluble in citrate of ammonia at 40° C.,	After hours.		Days.				
	12	14	3	4	8	10	14
	Per cent.		Per cent.				
	3.1	4.7	4.7	5.8	6.5	6.5	6.8

In another experiment they mixed 10 grams soil rich in lime, 2 grams superphosphate, containing soluble phosphoric acid 27 per cent., reverted, at 40° C., 21.7 per cent. Of total phosphoric acid present,

There became insoluble in citrate of ammonia at 40° C.,	After days.					
	3	5	6	8	10	14
	Per cent.					
In the shade,	4.1	5.4	5.4	...	6.8	7.4
In the sun,	11.1	15.4

In another experiment they mixed 10 grams clay soil, 2 grams superphosphate above used. Of the total phosphoric acid present,

There became insoluble in the shade, in the citrate of ammonia, temperature 40° C.,	Days.		
	3	8	14
	Per cent.		
	8.2	12.1	...

In another experiment with a sandy soil, same mixture. Of the total phosphoric acid present,

There became insoluble in citrate of ammonia, temperature 40° C., in the shade,	Days.		
	3	8	14
	Per cent.		
	4.	5.2	7.1

¹ Biedermann's Centralblatt, Feb. 1880, 84.

The authors, with Millot and Joullie, concluded from these experiments that the amount of phosphoric acid not dissolved by citrate of ammonia solution at 40° C. had become *insoluble phosphate of lime*; and so Déhérain¹ thought possibly oxide of iron and alumina produce insoluble phosphate of lime.

Had they digested these soils at the *temperature of 65° C.* *these discrepancies would have disappeared*, as is shown by experiments on soils 1, 2 and 3 (pp. 4, 5).

If all the reverted phosphoric acid present in these experimental mixtures had been in combination with lime, it would have been entirely redissolved at temperature 40° C. by the neutral citrate of ammonia solution, as is proved by Experiment No. 1 (p. 3), where lime was the only base present.

Therefore it is impossible to draw any other conclusion than that a portion of the phosphoric acid added was in *combination as reverted phosphates of iron and alumina in these soils*.

Thénard and Déhérain in 1858 believed that when even insoluble phosphate of lime was applied to the soil, eventually the phosphoric acid became combined with iron and alumina, through the chemical agencies of soils.

The physical conditions of oxide of iron and alumina in soils do not seem to affect the principal result of these comparisons of temperatures at which citrate of ammonia solution is used. The mineral brown hematite, used in Experiment No. 4 (p. 6), was chosen to represent the mineral oxides of iron formed by the decomposition of rocks; though much more active forms of these oxides, such as proto-compounds, are supposed to be present in the chemical changes going on in soils. Bauxite, used in Experiment No. 5 (p. 6), represents in the same manner the possible condition of alumina in soils. In short, I do not think that these minerals can be *more active* in their affinities for phosphoric acid than are those contained in soils.

Few deposits of mineral phosphates exist which are not contaminated with oxide of iron and alumina. Vast stores of phosphoric acid, provided by Nature for agricultural use, are represented by the following names of deposits:

¹ Annales Agronomique, Dec. 1880.

Commercial Name, ¹	Per cent. contents oxide iron and alumina.			
Wicken Coprolites, . . .				12.00
Cambridgeshire Coprolites, . . .	3.25	to		5.25
Bedfordshire " . . .	8.00	to		10.00
Ardennes " . . .	not mentioned			
Grand Pré " . . .	"			
Suffolk " . . .	4.75	to		10.50
Varennnes, " . . .	not mentioned			
Bellegarde " . . .	"			
Boulogne " . . .	6.00	to		11.50
Bordeaux " . . .	4	to		13
German Phosphorites, . . .	4.5	to		15
Russian " . . .	6			
Spanish " . . .	1.25	to		4
Oruba " . . .	14.5	to		26.50
Navassa Red, . . .	10	to		25
" Lower Flat, . . .	4	to		12
Sombrero, . . .	4	to		10
St. Martin's, . . .	2.75	to		4.50
Malden Island, . . .	1			
South Carolina (land) . . .	7			

The last is now sold in market, colored a pronounced reddish tint by the oxide of iron it contains. It is evident that superphosphates made from such minerals are undervalued when the reverted phosphoric acid is estimated at a temperature of 40° C.; because, as is fair to conclude from Experiments 2, 3, 4 and 5 (pp. 5, 6), the oxides dissolved by the sulphuric acid subsequently combine in the superphosphate with their equivalent of phosphoric acid, and the reverted phosphates of iron and alumina thus formed are not *all dissolved at the temperature of 40° C.*; whereas, a slight increase in temperature dissolves them entirely, without unduly attacking the *insoluble* mineral, as is proven by my experiments on raw phosphates (p. 3).

Millot² showed the result of contact of these oxides with soluble phosphates in a superphosphate prepared from coprolites of the Ardennes. All the phosphoric acid was soluble in water when freshly made, but after two years 90 per cent. of the phosphoric acid was insoluble in water. Millot washed this with hot water until

¹ Spons' Encyc.² Comptes Rendus, 78, 1134; 82, 522.

all the gypsum was removed, and found the residue to be *free from lime* and to consist of phosphate of iron.

The experiments of Dr. E. Heyden¹ show how very rapidly and completely reversion takes place under conditions more nearly similar to those when fertilizers are applied to fields. He filtered solutions containing an equal amount of phosphoric acid through four separate soils; 2500 cc. of the solutions to each 1250 grams of the soils.

	Amount Reverted.	Amount Soluble.	Per cent. not Reverted.
Soil A, surface soil within 8" of surface. }	.137 gram	.0057 gram	4.16
Soil A, subsoil, between 8" and 16". }	.147	.0026	1.76
Soil B, surface, within 8" of surface. }	.165	.0053	3.21
Soil B, subsoil, between 8" and 16". }	.153	.0019	1.24

Dr. Stohman² showed by his experiments that from a *dilute* solution of salts, filtered through a given mass of soil, a larger per cent. was removed than from a more concentrated solution. One thousand pounds of superphosphate, containing one hundred pounds of soluble phosphoric acid, sown upon an acre of land, represent a distribution of only 0.0005 gram to every 26.7 grams of soil, which is the weight of a mass 1 sq. inch in surface and 3 inches deep. In the experiments of Heyden, just quoted, 0.150 gram P_2O_5 was used to 1250 grams of soil, or about 0.0035 gram to every 26.7 grams of soil. In my experiments 0.071 gram P_2O_5 was used to 25 grams of soil. Thus in actual field practice a solution is employed which, proportionately to the soil, is seven times more dilute than that which Heyden experimented with, and about one hundred and twenty times more dilute than that used in my experiments. It is probable, therefore, that the superphosphate becomes reverted *on the spot* where it is sown. If spread broadcast, it lies near the surface; if harrowed or plowed under, it is brought a few inches deeper. Liebig³ analysed samples of soil at the experiment station at Rothamsted which had received dressings of superphosphates for twenty-two years in succession, and found three-fourths of the phosphoric acid in the first nine inches of soil.

¹ Annalen der Landwirtschaft, 45, 189.

² Henneberg's Jour. f. Landwirtschaft, 1862.

³ Roy. Ag. Soc., June, 1881.

In conclusion, it is evident, from the *marked* and *positive* results of the foregoing experiments, that the only *equitable* method of valuation of the *reverted phosphoric acid* of a *superphosphate* must be based upon these facts.

I assert, therefore, that the true method of analysis is that which dissolves reverted phosphates of the same degree of solubility as those which are formed when a soluble superphosphate is mixed with the soil;

That the value of a superphosphate is determined, not alone by its condition in the storehouse, but by its condition within a reasonable time after being sown upon the field;

That phosphates, soluble in water, become, within a few hours, entirely reverted in some cases, in others to the extent of over 90 per cent. This has been shown by my experiments with artificial and natural soils; and there is no lack of testimony by most eminent authorities in verification of these results;

That a superphosphate which was valued by a method in which the temperature was 40° C., if re-analysed by the same temperature after several days' contact with the soil, would show, after allowing for the amount previously in the soil, an apparent loss of 20 to 30 per cent. of available phosphoric acid, as has actually been shown by Experiments 1, 2 and 3 (pp. 8, 9).

The following method of analysis of superphosphates recognises the principles demonstrated in this and the previous papers, and contains in addition a detailed manipulation which long experience has fully recommended to our confidence.

Method of Analysis of Superphosphates.

Preparation of Sample.—Pass the sample¹ through a twelve-mesh sieve.

Moisture.—Dry 5 or 10 grams at 100° C.

Total Phosphoric Acid.—Weigh 2 grams, brush into a 200 cc. flask, add 50 cc. nitric acid,² boil gently for 15 minutes, cool, fill to mark, mix, filter through a dry filter-paper into a dry receiver, take 50 cc. of filtrate, place in a beaker, add 25 cc. conc. ammonia, then nitric acid to acidity. To the hot liquid add *molybdic solution*, let stand

¹ If too wet, a portion of the sample must be air-dried and then sifted, and an allowance made by calculation for loss of moisture.

² Several cubic centimeters of HCl must be added here, and in solution of the insoluble when working with difficultly soluble iron and alumina phosphates.

for one hour at about 65° C., filter, wash with *nitrate of ammonia* solution, dissolve on paper with hot *ammonia solution*, and wash with same. Run in *magnesia mixture* from a burette at the rate of one drop a second, stirring constantly. Let stand several hours, filter, wash with *ammonia solution*, dry, ignite to whiteness and weigh.

Soluble Phosphoric Acid.—Weigh 2 grams, rub up in a mortar with a soft *rubber-tipped* pestle,¹ digest in 25 cc. of cold water, decant clear liquid into a filter-paper, filtering into a 200 cc. flask, add 25 cc. of water to residue, digest for several minutes and again decant. Repeat for five or six times, and finally bring all upon the filter-paper and wash till flask is filled to the mark. Mix, take 50 cc. and estimate P_2O_5 as in total.

Insoluble Phosphoric Acid.—Wash the residue upon the paper into a 200 cc. flask with 100 cc. *citrate solution*, cork the flask with a common cork, digest in a water-bath at constant temperature 65° C. (150° F.) for thirty minutes, with frequent agitation. Filter the warm solution quickly,² and wash with cold *water*. Return paper and contents to the same 200 cc. flask, add 50 cc. nitric acid, boil for fifteen minutes and estimate the P_2O_5 as in total.³

Reverted Phosphoric Acid.—The soluble + insoluble phosphoric acid subtracted from the total will give the reverted phosphoric acid.

Memoranda.

Molybdic Solution.—This is made up as usual to contain 5 per cent. MoO_3 . Of this use 60 cc. to every 0.100 gram P_2O_5 . (The filtrate should be tested by addition of phosphate soda, to see that an excess of precipitant is employed.)

Magnesia Mixture.—Make up as follows:

110 grams cryst. magnesium chloride,
300 grams ammonium chloride,
400 cc. conc. ammonia,
1500 cc. water.

¹ This serves simply to break up lumps. No grinding nor trituration of sample is made either in extraction of soluble or reverted phosphoric acid.

² This is best accomplished by use of a filter-pump, or by use of plaited filter-paper. After the citrate solution has run through, the first paper may advantageously be rolled up, placed upon a second paper and washed. The use of citrate solution for washing is discarded as being equivalent to further treatment.

³ The organic matter from the paper does not interfere in the least with the estimation. We have never found soluble silicic acid in any phosphate in sufficient quantity to give a precipitate and thus interfere with the accuracy of the above method.

Use 10 cc. to every 0.100 gram P_2O_5 .

(15 cc. added to 100 cc. *ammonia solution*; must remain clear after standing twenty-four hours.)

Citrate Solution.—Made up to sp. gr. 1.09 carefully neutralised.

Ammonia Solution.—This consists of one part strongest ammonia to three parts water.

Nitrate of Ammonia Solution.—This is a 10 per cent. nitrate of ammonia solution slightly acidified with nitric acid.

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THE DETERMINATION OF THE FLASHING POINT OF PETROLEUM.

BY JOHN T. STODDARD.

In a recently published paper¹ on this subject, Beilstein reviews the method proposed by me last year,² and reaches some conclusions so different from mine that I have been led to repeat my former experiments and to subject the method to a still more thorough investigation.

The method is a modification of that due to Liebermann,³ and consists in testing a mixed current of air and petroleum vapor, obtained by forcing air through petroleum, as it issues from the mouth of a cylindrical oil holder. Having found that a continuous current of air gives results which are nearly identical with those obtained by the intermittent current employed by Liebermann, I proposed the substitution of the former on account of the greater uniformity of the results and the increased simplicity of manipulation. Beilstein concludes from his experiments with the tester that the use of a continuous current of air "must lead to entirely wrong results," as, he writes, Liebermann had already pointed out. It is, however, noteworthy that while Liebermann⁴

¹ Zeitschrift für analytische Chemie, **22**, 309.

² Zeitschrift für analytische Chemie, **21**, 321.

³ This Journal, **4**, 285.

⁴ *Loc. cit.*

foregoes the use of the continuous current because he finds from his experiments that it *raises* the flashing point, Beilstein's objection to it is that it gives *too low* a result.

Two series of experiments are given as the basis of this conclusion. In one series the sample of oil was kept at a constant temperature, while air was forced through it and a small flame held at the mouth of the cylinder until the flash took place, if at all. The results obtained are :

Time before flash,	3 sec.	5	6	8	11	41
Temperature of oil,	29.1°	28.7	28.3	27.8	27.2	26

At 25.3° no flash occurred, even after six minutes.

In consequence of this evident dependence of the result upon the duration of the air current, five seconds was chosen as the normal (?) time in the second series of experiments, which show that the oftener the test is repeated, *i. e.* the more air that is led through the oil while it is heated, the lower is the temperature at which the flash takes place. Oil which on direct heating did not flash below 28.7° was tested through different ranges of temperature by leading air and holding the flash jet at the mouth of the holder for five seconds at each degree, with the following results :

Beginning at	11°	12	18	24	26	27
Oil flashed at	27.3°	27.2	27.7	28.3	28.2	28.7

My experiments on the influence of duration of air current on the flashing point confirm the results given by Beilstein; but at the same time show that the interpretation of them which leads him to the arbitrary choice of a normal interval is quite gratuitous. It will be noticed in the results which he gives, that the lower the temperature at which the oil is held, the longer is it necessary to continue the air current in order to obtain a flash, until finally at 26° a minimum flashing point is reached, below which no flash is obtained even after six minutes; and this too in spite of the demonstration which follows in the second series of results that the flashing point is lowered by increasing the quantity of air led through the oil.

My results, some of which are given below, also indicate clearly that a minimum is reached after the air has run through the oil thirty to sixty seconds; while further experiments (see II) show unmistakably that longer continuance of the air tends to slowly *raise* the temperature at which the oil will flash.

I. *Influence of duration of air current on the flashing point of oil held at a constant temperature.*

1. Time before flash,	3 sec.	30	55	35	42	60 ¹	82 ¹	no flash.
Temperature of oil,	36.8°	36.2	36	36	36	35.9	35.7	35.4
2. Time before flash,	27 sec.	30		48		65	36	no flash.
Temperature of oil,	36°	35.7		35.6		35.6	35.6	35.4
3. Time before flash,	15 sec.			60		40		no flash.
Temperature of oil,	28.3°			27.6		27.6		27.2

II. *Influence of quantity of air led through the oil as it is heated.*

1. Time of continuous air current,	2.5' min.	3	5	12	
Flashing point,	35.3	35.4	35.5	36.3	
2. Air led for 5 sec. at each degree, and when near the flashing point every 0.2°-0.3° :					
Beginning at,	45°	40	36	27	16
Flashing point,	47.6°	47.7	47.4	47.8	48

These last results lead, as has already been indicated, to an opposite conclusion from that reached by Beilstein. That a higher flashing point should be the result of increasing the quantity of air led through the oil is, however, what one would naturally expect; for the more volatile portions are being continually removed by the air current—more rapidly, of course, as the temperature rises—and thus the flash must occur at a higher point, unless the amount of oil with respect to that of air is large.

In none of the experiments which Beilstein gives on this point, however, can the quantity of air have been large enough to appreciably raise the flashing point, as is shown by II (in the determination which began at 11° and resulted in a flash at 27.3° the air is equivalent to a continuous current for $18 \times 5 = 90$ sec.); and the only explanation of his figures, it seems to me, must be found in the irregularity of the results which, in my experience, always attends the use of the intermittent method. This irregularity of results, and also the fact that the intermittent method gives higher flashing points than the continuous—which, indeed, is evident from I.—is shown by the following.

¹ After several abortive flashes which heated the sides of the holder.

III. *Comparison of the intermittent and continuous methods.*¹

Flashing points determined by the

	1.	2.	3.
5 sec. method, . . .	47.7°	36.8, 37	37.1, 36.8, 36.5, 36.6, 36.8
Continuous method,	46.4	35.6, 35.7, 35.7	36.1

I am also unable to agree with the interpretation which is given of experiments with oil cylinders of different dimensions. Everything depends, according to Beilstein, on the ratio of diameter to length of cylinder. Concordant results can only be obtained when the length is 5-7 times the diameter. If these limits are observed, it makes no difference to what height the cylinder is filled with oil.

It will be seen by reference to the determinations given below, that the flashing point depends, not upon the dimensions of the *cylinder*, but upon the dimensions of the *vapor space* above the surface of the oil. Cylinders of the same diameter and different lengths all give the same flashing point when filled to the same distance from the top. Indeed, this follows as a necessary corollary to the fact established by Liebermann,² that the quantity of oil does not affect the determination; for difference in length of cylinder in this case means simply difference in the quantity of oil employed in the test.

IV. *Determinations made in cylinders of different dimensions.*

"Vapor space" = distance from foam to mouth of cylinder.

1. Vapor Space.	Dimensions of Cylinders.				
	2 × 10 cm.	2 × 16	2 × 20	2 × 30	2 × 40
5 cm.	32.7°	32.8	32.7	32.6	32.5
9		33.5	33.5	33.5	33.6
15			34	33.7	34
20				35	{ 34.9 34.6

2. Vapor Space.	Dimensions of Cylinders.			
	3 × 12 cm.	3 × 18	2.7 × 32	3 × 43
7 cm.	35.7°	35.7	35.7	35.9
12.5		36.8	36.6	36.2
18			36.9	36.7

¹ Cf. also this Journal, *loc. cit.*

² *Loc. cit.*

V. *Influence of length of vapor space.*¹ 1. Cylinder 3 × 43 cm.

Vapor space,	4 cm.	7	11	15	18	19	25	30	33	36	38
Flashing point,	35.9°	36.3	36.7	37.1	37.2	37	37.6	38.4	38.2	39	39.8

2. Cylinder 4.7 × 25 cm.

Vapor space,	5 cm.	6.5	9.5	13	18
Flashing point,	43.5	43.8	44.3	45	47

VI. *Comparison of results obtained from cylinders of different diameters.* Vapor space in each case 5 cm.

Diameter,	2 cm.	2.7	3	4	4.7	6.5
Flashing point,	43.4°	43.6	43.2	42.8	43.1	42.9

The flashing point rises as the distance from the top of the foam to the mouth of the cylinder is increased. Diameters greater than 2.5 cm. scarcely affect the determination when this distance is less than 6 cm. The quantity of oil must not be too small, else the results will be unreliable—higher and somewhat irregular—on account of loss of vapor carried away by the air current before the flashing point is reached. My recent investigation has led me to fix 50 cc. as the minimum quantity of oil which should be used for a determination. The cylinder which serves as oil holder must, therefore, be large enough to contain at least this quantity of oil, and leave a distance of some 6–4 cm. for vapor space. With this larger quantity of oil a stronger current of air than that previously recommended is necessary, and I agree with Beilstein that the current should be strong enough to maintain at least 1 cm. foam on top of the oil.

The aim of this method of testing is to find the *lowest* flashing point which can be accurately determined. It is the outgrowth of the valuable suggestion of Victor Meyer,² who thought by saturating air with petroleum vapor to determine the “absolute flashing point”; and although it cannot, perhaps, be claimed that this is accomplished, we certainly have in the method a means of near approximation to this point.

The obvious importance of obtaining a minimum flashing point appears to have been entirely overlooked by Beilstein, who seeks only for concordant results, and, in the modification he proposes, takes as the flashing point a temperature higher than that given by the preliminary test.

¹ Cf. also this Journal, *loc. cit.*² Wagner's Jahresbericht, 1879, 1175.

In the practical employment of a method for testing the safety of petroleum, it is also in the highest degree important that the determination be free, as far as possible, from arbitrary conditions, and that both apparatus and manipulation be of such simplicity that reliable results can be obtained without the necessity of especial skill or experience. It is believed that the apparatus and method described below leave little to be desired in these essential particulars.

1. The oil cylinder should have a diameter of at least 2.5 cm. A diameter of more than 4 cm. is not advisable, because of the large quantity of air which is then required in making the determination (cf. 4). The cylinder may have any convenient length, provided it holds, when filled for the test, not less than 50 cc. of oil. With 2.5 cm. diameter the length should be at least 16 cm.

2. The cylinder is filled with oil to a point such that, when the air is running, the surface of the foam is about 5 cm. from the top.

3. The oil holder is heated in a water-bath in which it sinks to the level of the oil. The temperature should not rise, when approaching the flashing point, faster than 2° a minute.

4. Air is forced through the oil with such velocity that not less than 1 cm. foam is maintained on its surface, and a flash jet brought to the mouth of the cylinder for about one second every 0.5° or oftener in the vicinity of the flashing point. The approach of the flashing point is announced by the appearance of a blue halo of burning vapor about the flame, which is larger at each trial until at last it detaches itself from the flash jet and runs down to the surface of the oil.

The test is now repeated with a fresh sample of the oil, and the air current started not less than one and not more than three to four minutes before the flash. It is a good plan to let a very slow current of air bubble through the oil from the time the tester is put into the water-bath, so as to secure regularity in the heating.

I have usually employed as flash jet a gas flame from the tip of a blowpipe, and about 0.5 cm. long. The size of the flame makes, however, very little difference in the results.

All the temperatures given are in centigrade degrees, and all the determinations were made with a thermometer graduated in 0.2° .

HAYDENITE.

BY H. N. MORSE AND W. S. BAYLEY.

Haydenite, which is found in the gneiss quarries near Baltimore, where it is associated with beaumontite and stilbite, was first discovered by Dr. Hayden of Baltimore.

Cleaveland¹ afterwards described it, though apparently with considerable hesitation, as an independent species, and gave to it the name of the discoverer. In consequence of its resemblance to chabazite, however, its independence as a species was generally doubted, until Levy² examined the mineral crystallographically, and found it, as he supposed, to be monoclinic. Levy was afterwards shown to be in error by J. D. Dana,³ who ascertained that the crystallisation of haydenite is in reality rhombohedral, and that the crystals are scalenohedrons. On crystallographic grounds, as well as from a consideration of the physical properties, Dana concluded that haydenite and chabazite are identical, notwithstanding the fact that the analytical results thus far recorded could not be reconciled with this view. The probability of the identity of the two has been further strengthened by the results of the recent optical examination of haydenite by Des Cloizeau.⁴

Up to the present time two analyses of haydenite have been published—one by B. Silliman, Jr.,⁵ the other by Delesse.⁶ The results obtained differ very widely, and are in neither case reconcilable with what is generally believed to be the typical composition of chabazite.

Under the circumstances it seemed quite desirable that further chemical analyses of the mineral should be made, and having at our disposal a quantity of apparently undecomposed material, we have carefully determined the various constituents. It was found on making a qualitative examination of different specimens, that barium is a constant constituent of the mineral—a fact which had escaped the observation of those who have previously analysed it.

¹ Mineralogy, 2d ed. 478.

² L'Institut, 1839, **313**, 455; Berzelius' Bericht, **20**, 217.

³ Am. Journal of Science, (2) **17**, 82.

⁴ Bulletin Soc. Min. de France, 1881; Jahrbuch für Min. u. s. w., 1883, 6.

⁵ Am. Journal of Science, **46**, 379.

⁶ Revue Industr. et Scient. **25**, 107; Berzelius' Bericht, **27**, 248.

We give below the results obtained by Silliman and Delesse, and, afterwards, those found by ourselves :

	Silliman.	Delesse.
Silica,	56.831	49.5
Alumina,	12.345	23.5 { Al_2O_3 Fe_2O_3
Ferrous oxide,	8.035	
Lime,	8.419	2.7
Magnesia,	3.960	trace
Potash,	2.388	2.5
Water,	8.905	21.0
	<hr/>	<hr/>
	99.882	99.2

	I.	II.	Average.
SiO_2 ,	49.29	49.19	49.24
Al_2O_3 ,	18.06	18.07	18.07
Fe_2O_3 ,	0.79	0.88	0.84
CaO ,	5.13	5.19	5.16
MgO ,	0.86	0.86	0.86
BaO ,	1.46	1.48	1.47
MnO ,	trace	trace	...
K_2O ,	3.16	2.84	3.00
H_2O ,	21.31	21.31	21.31
	<hr/>	<hr/>	<hr/>
	100.07	99.81	99.95

If we suppose the small amount of iron found in these analyses to be in the ferrous condition, and therefore, like magnesium and barium, as replacing calcium, and remember that the alkali in chabazite varies within quite wide limits, we find that the results obtained agree with the formula of Rammelsberg for chabazite, quite as closely as those of the more reliable recorded analyses of that mineral. We believe, therefore, that haydenite is in its chemical composition, as well as in its crystallisation and physical properties, identical with chabazite.

Contributions from the Sheffield Laboratory of Yale College.

XVII.—ON THE REDUCTION OF BENZOYL-ORTHO-NITRANILIDE.

BY W. G. MIXTER.

Hübner¹ obtained by the action of tin and hydrochloric acid on benzoyl-o-nitranilide, benzenylphenylenamidine, $C_{13}H_{10}N_2$. Other reduction products of this ortho-nitranilide do not appear to have been made. It has been shown² that para and meta nitranilides yield, when treated with zinc and ammonia, azo and amide bodies, and the following results show the formation of analogous ortho compounds.

Ortho-azoxybenzanilide.

Pure benzoyl-o-nitranilide, prepared from pure o-nitraniline and benzoylchloride, was dissolved in alcohol and pulverised zinc, ammonia and platinic chloride were added. There slowly separated from the solution a yellow fibrous mass, which was filtered off, washed with alcohol, dilute acid, and lastly with water. It was dried at 100° C. The analyses given are of two different preparations.

I. 0.3007 gram yielded 0.7867 gram of CO_2 and 0.1265 gram of H_2O . 0.3175 gram yielded 36.1 cc. of N at 21° C. and 766 mm. pressure.

II. 0.344 gram yielded 0.9098 gram of CO_2 and 0.1466 gram of water. 0.3075 gram yielded 33.9 cc. of N at 19.6° C. and 760 mm. pressure.

	Calculated for $C_{26}H_{20}N_4O_3$.	I.	II.
C	71.56	71.35	72.12
H	4.58	4.67	4.73
N	12.85	13.36	12.93

The ortho-azoxybenzanilide, $\begin{array}{c} C_6H_4NHC_7H_5ON \\ | \\ C_6H_4NHC_7H_5ON \end{array} \diagup \diagdown O$, has a bright yellow color, is insoluble in water and sparingly soluble in boiling alcohol, and melts at 195° C. Attempts were made to remove the benzoyl group by potassium hydroxide and by sulphuric acid, but ortho-azoxyaniline was not obtained.

¹ Annalen der Chemie, **208**, 302.

² This Journal, **5**, 1, p. 282.

Benzoyl-ortho-phenylenediamine.

The alcoholic ammonia solution filtered from the azoxybenzanilide was evaporated to dryness, and the residue was digested with a large quantity of boiling water. The clear aqueous solution on cooling yielded minute crystals which melted at 140° C., and gave the following analytical results:

0.2545 gram yielded 0.676 gram of CO_2 and 0.128 gram of H_2O .

0.1447 gram yielded 16.55 cc. of N at 18.6° C. and 757.7 mm. pressure.

	Calculated for $\text{C}_6\text{H}_4\text{NHC}_7\text{H}_5\text{ONH}_2$.	Found.
C	73.58	72.44
H	5.66	5.59
N	13.30	13.19

The substance appears to be a benzoylphenylenediamine, of which the para and meta modifications are known. The ortho modification, so far as the writer is aware, has not been described. In order to obtain a more satisfactory quantity of this body for analysis, and also for comparison, an attempt was made to prepare it by reducing benzoyl-o-nitranilide with alcoholic ammonium sulphide. The solution, after standing a day, was evaporated to dryness, and the residue was digested with hydrochloric acid. The base was precipitated from the acid solution by ammonia, washed and dried at 100° C.

I. 0.3145 gram yielded 0.8483 gram of CO_2 and 0.1588 gram of H_2O .

II. 0.3294 gram yielded 0.8873 gram of CO_2 and 0.1643 gram of H_2O .

III. 0.1508 gram yielded 17.42 cc. of N at 19° C. and 760 mm. pressure.

	Theory.	I.	II.	III.
C_{13}	73.58	73.56	73.46	
H_{12}	5.66	5.61	5.56	
N_2	13.30			13.56
O	7.46			

The substance is nearly white, is freely soluble in alcohol, and melts at 140° C. It dissolves in warm oil of vitriol, and the solution gives off benzoic acid slowly. Platinic chloride precipitates a slimy salt in an aqueous solution of the hydrochloride. 21.89 per cent. of platinum was found in the salt, which was dried at 100° C.; theory

requires 23.77 per cent. of platinum in $C_6H_4NHC_7H_5ONH_2H_2PtCl_6$. 21.73 per cent. of platinum was found in the platinum salt of the benzoyl-o-phenylenediamine obtained in the reduction with zinc and ammonia. The platinum salt is very soluble in alcohol and tolerably soluble in water. A complete analysis of the platinum salt was impossible, owing to lack of substance.

The mother-liquor from the crystals of benzoyl-phenylenediamine obtained in the reduction by zinc was evaporated, and the residue was dissolved in hydrochloric acid. The base was precipitated by ammonia and analysed with the following results:

	Calculated for $C_{13}H_{10}N_2$.	Found.
C	80.41	77.92
H	5.16	5.13
N	14.43	14.58
	<hr/> 100	<hr/> 97.63

The analysis shows that nearly all the oxygen had been removed from part of the benzoyl-nitranilide, and indicates the possible formation of benzenylphenylenamidine, $C_{13}H_{10}N_2$. It may be mentioned that no azobenzanilide was obtained.

HEPTANE FROM PINUS SABINIANA.¹

By C. SCHORLEMMER AND T. E. THORPE.

In the last communication made by one of us on this subject² it was stated that we contemplated making a joint investigation on the heptane from *Pinus Sabiniana*. A large quantity of the pure heptane was treated with chlorine in the manner described in this series of communications,³ and the chlorides boiling between 143° and 157.5° were converted into the alcohols in the ordinary way. The primary alcohol boiled between 165° – 170° ,

¹ Communicated by the Authors from the Philosophical Transactions of the Royal Society, Part I, 1883.

² Philosophical Transactions, 1880, p. 451.

³ Philosophical Transactions, 1872, p. 111; and this Journal, 1, 155.

whilst the secondary alcohol distilled over, for the most part, between 156° – 158° . The alcohols were then oxidised in the manner described in the Philosophical Transactions, 1872, p. 121. The ketone obtained from the secondary alcohol was further oxidised by being heated with the chromic acid solution in sealed tubes at 100° . The liquid was then neutralised and the unattacked ketone was separated by distillation. In order to isolate the acids contained in the residue, small quantities of sulphuric acid were added, and the acid which separated out (pentoic acid) was distilled off in a current of steam—the operation being repeated until the pentoic acid was no longer recognisable by its smell. The acetic acid contained in the residue was then separated by a further addition of sulphuric acid and distilled off by direct heating. The respective silver salts of the two acids were then prepared from the several fractions in the ordinary way. Analysis showed that the separation of the acids was complete.

I. Silver salt from the normal alcohol.

(a) 0.4035 gram salt gave 0.1842 gram Ag = 45.6 per cent.

(b) 0.210 “ “ 0.0953 “ = 45.4 “

Calculated for silver heptate 45.5 per cent.

II. Silver salts from ketone from secondary alcohol.

0.2022 gram salt A gave 0.1050 gram Ag = 51.9 per cent.

0.1491 “ “ 0.0771 “ = 51.7 “

Silver pentoate = 51.6 Ag.

0.235 gram salt B gave 0.1518 gram Ag = 64.59 per cent.

Silver acetate = 64.67 per cent.

The results of the oxidation show therefore that primary heptyl alcohol and methyl-pentyl-carbinol had been formed, as in the case of heptane from petroleum.

Another portion of the mixture of the monochlorides was then heated to 100° with alcoholic solution of potash, whereby in addition to heptylene a mixture of the ethyl heptyl ethers was obtained. The heptylene, purified by repeated rectification over sodium, boiled constantly at 98.5° . It was placed in contact with an excess of fuming hydrochloric acid in the dark and in a well-closed bottle for six weeks. Heptylene from petroleum heptane was similarly treated.

Now it is remarkable that whilst hexylene from mannite combines completely with hydrochloric acid under these circumstances forming secondary hexyl chloride,¹ the greater part of the heptylene

¹ Philosophical Transactions, 1880, p. 457.

from *Pinus* heptane was found to be unattacked, not more than 10 per cent. of heptyl chloride having been formed. On the other hand, about one-half of the heptylene from petroleum had been converted into the chloride in accordance with the former observations made by one of us on this point.

The uncombined portions of both specimens of heptylene were again placed in contact with the fuming acid, and (the research being interrupted by other work) they were allowed so to remain for many months. At the expiration of this time it was found that the *Pinus* heptylene had united almost completely with the acid, whilst an additional quantity of the heptylene from petroleum had likewise entered into combination. It follows from this that, contrary to expectation, hydrochloric acid acting in the cold is not capable of effecting the separation of isomeric paraffins.¹

It is remarkable that the *Pinus* heptylene should require so long a time to bring about its union with hydrochloric acid, since, as will be shown immediately, its constitution is exactly analogous to that of the hexylene from mannite or propyl-methyl ethylene, $C_3H_7.CH=CH.CH_3$, which so easily goes into combination.

In order to establish the constitution of the heptylene from *Pinus* it was oxidised by means of a solution of potassium dichromate in dilute sulphuric acid in the manner adopted by Hecht in the oxidation of hexylene from mannite.² The acids so formed were converted into the silver salts and analysed with the following results :

Fraction.	Salt taken.	Silver found.	Silver pentoate 51.67.
1	0.0855	0.0443	51.81
2	0.0560	0.02875	51.34
3	0.1140	0.0590	51.75
4	0.1350	0.0700	51.84
5	0.0685	0.0350	51.09
6	0.1000	0.0540	54.00
7	0.2200	0.1370	62.27
8	0.1370	0.0855	64.60
9	0.1400	0.0910	65.00

Silver acetate 64.67.

The first five fractions consisted of a fine crystalline powder, the last three were glistening needles.

These observations clearly indicate that only pentoic and acetic acids had been formed by the oxidation, and therefore that

¹ Philosophical Transactions, 1880, p. 451.

² Berichte der deutschen chemischen Gesellschaft, **11**, 1152.

the *Pinus* heptylene is pure butyl-methyl-ethylene, $C_4H_9.CH = CH.CH_3$, which had been formed from the secondary heptyl chloride, $C_4H_9-CH_2-CHCl.CH_3$.

The results, taken in conjunction with those of former investigations, leave no doubt, therefore, that by the action of chlorine upon a normal paraffin, not all the chlorides indicated by theory are formed, but only the primary and a secondary chloride which contains the group $-CHCl.CH_3$. One of us has formerly shown that by the action of bromine upon normal paraffins from petroleum only secondary bromides corresponding to chlorides are formed.¹ Venable has since shown that *Pinus* heptane is acted upon in the same way.²

ON SOME NEW FORMS OF ALBUMOSE.³

BY W. KÜHNE AND R. H. CHITTENDEN.

At the end of our recent paper "on the primary cleavage products of the albumins,"⁴ we mentioned the possibility of hemialbumose being a mixture. This idea was suggested to us, first, by the circumstance that all the specimens of hemialbumose which we had prepared yielded by the action of peptone-free trypsin, more or less peptone together with the amido-acids; and, secondly, by certain differences in the solubility of the albumose of different preparations. If the first of these considerations could be overlooked, the second, which we have called particular attention to by the terms "soluble" and "insoluble" hemialbumose, might likewise be considered of little importance, especially when it is remembered that the question as to whether the albumins are really bodies soluble in water has not yet been satisfactorily answered. And as it is often questioned whether the apparent solubility of the albuminous bodies does not depend upon the presence and action of non-removable salts, or of combined acids

¹ Philosophical Transactions, 1878, Part 1, p. 49.

² Berichte der deutschen chemischen Gesellschaft, 13, 1649.

³ An abstract of this paper was read before the National Academy of Sciences, in November, 1883.

⁴ Zeitschrift für Biologie, 19, 159.

or alkalis, so in a similar manner the solubility of hemialbumose might under certain circumstances be considered only as apparent. We have therefore hitherto overlooked this point, and confined ourselves in the preparation and selection of products for study to the following reactions which we deemed characteristic of hemialbumose: 1. In distinction from the albumins: (*a*) solubility in boiling water, in boiling dilute salt solutions even when slightly acidified, with eventual reprecipitation as the solution cools; (*b*) unaltered solubility after precipitation with strong alcohol. 2. In distinction from peptones: (*a*) very slow or imperfect dialysis; (*b*) precipitation by sodium chloride or by sodium chloride and acetic acid, or coagulation at temperatures far below 70° C., with or without the addition of salt and acid, together with solution of the coagulum at temperatures above 70° C. and by boiling. 3. In distinction from the bodies belonging to the anti-group of albumins: decomposition by trypsin with formation of leucin, tyrosin and a body colored violet by bromine. The analyses of hemialbumose showed a content of carbon not over 52.29 per cent. and not under 49.82 per cent.; with an average for hemialbumose from fibrin, the products of which alone will be considered in the present article, of carbon 50.32 per cent.

We had obtained hemialbumose characterised in this manner from coagulated egg-albumin, from the albuminous matter of serum and from fibrin, in part by boiling with diluted sulphuric acid and in part by pepsin digestion; a similar albumose was likewise found present in the urine of a person with osteomalachia. In the preparation of the albumose, one portion of "soluble" albumose was generally obtained, which together with the peptones was dissolved from the alcohol precipitate by cold water; and, secondly, an "insoluble" portion, which was entirely freed from peptones by washing with cold water. The soluble portion was then separated from peptone by boiling with an excess of sodium chloride and some acetic acid. The insoluble portion was purified by solution in boiling water, reprecipitation in the cold, eventually with the aid of alcohol.

In addition to the differences of solubility we noticed later the occurrence of an inconstancy in the reactions, viz. with reference to precipitation of the albumose by sodium chloride; and this led to the method of separation about to be discussed, by which *four* different forms of albumose were isolated from the filtrate

obtained from the neutralisation precipitate in the digestion of fibrin. These are:

No. I. Precipitated by excess of sodium chloride in substance, soluble in cold and hot water.

No. II. Precipitated by excess of sodium chloride, insoluble in cold and in boiling water; but, on the other hand, soluble both in dilute and strong solutions of sodium chloride.

No. III. Similar to No. II, but insoluble in solutions of sodium chloride.

No. IV. Not precipitated by excess of sodium chloride, but precipitated by sodium chloride and acids; soluble in pure water.

On these specific grounds we name No. I. *Protalbumose*; No. IV. *Deuteroalbumose*; No. II. *Heteroalbumose*; No. III. *Dysalbumose*; the "hemi" being retained in each case.

These bodies were obtained in part by digestion of fibrin with pepsin-hydrochloric acid, or from the commercial "pepton" manufactured by Witte, and in part from preserved hemialbumose from the urine of a patient with osteomalachia.

Preparation of the different forms of albumose by pepsin digestion.

1500 grams of raw fibrin were placed in 5 litres of 0.4 per cent. hydrochloric acid for twenty-four hours. The swollen mass was then warmed to 45° C., after which 400 cc. of normal gastric juice¹ were added, and the mixture kept at the same temperature for one hour with frequent stirring. After filtering through a hair sieve to remove the small residue of fibrin, the turbid fluid was brought to the faintest possible alkaline reaction with sodium hydroxide and then filtered from the abundant neutralisation precipitate. The clear filtrate was rubbed up with a quantity of sodium chloride, sufficient to insure a slight excess of salt in the abundant white precipitate. The precipitate was washed first upon the filter, with some saturated solution of sodium chloride, then removed from the filter and washed in the most thorough manner possible by trituration with the salt solution. This precipitate contained prot-, dys- and heteroalbumose. From the united filtrates saturated with sodium chloride, deuteroalbumose separated out on the addition of a suitable quantity of 30 per cent. acetic acid in which sodium chloride had been previously dissolved. This precipitate

¹ Compare *Zeitschrift für Biologie*, 19, 184.

was less easily collected upon a filter owing to its tendency to form a resinous gum. In the filtrate only traces of albumose were found when the proper quantity of acetic acid had been added ; in case the fluid had not been sufficiently acidified, separation of the remaining albumose was accomplished by the addition of more acid, or in case too much acid had been added the excess was easily removed by partial neutralisation. When a good separation had been made there was usually, however, sufficient albumose in the filtrate to yield a turbidity with a little nitric acid, or after boiling the solution, in which case no coagulation was observed, the concentrated solution freed from the deposited salt yielded a small quantity of deuteroalbumose on the addition of a fresh quantity of acetic acid. After this precipitation nothing was found in the residue other than a small quantity of peptone.

The first precipitate produced by sodium chloride alone and freed as completely as possible from the salt solution by pressure was not wholly soluble in water, and its insolubility increased the larger the quantity of water employed. But as it was also not completely soluble in sodium chloride solution of from 1 to 10 per cent., we concluded that this precipitate contained besides a body soluble in water, a second body soluble only in salt solution, and also a third, soluble in neither water nor sodium chloride. The latter (dysalbumose) was obtained as an insoluble residue by simple filtration, trituration and washing first with 5 per cent. sodium chloride solution, and finally with water. The second (heteroalbumose) separated as an insoluble gummy mass by dialysing the salt solution until the chlorine had entirely disappeared, while the first (protoalbumose) remained alone in the solution.

In testing the protoalbumose for the presence of any traces of the other three bodies, which was accomplished by a repetition of the whole process applied to the dialysed and filtered fluid freed from heteroalbumose, or to the substance precipitated by alcohol, it was found that both hetero- and dysalbumose were absent, but that deuteroalbumose was present to the extent of nearly 50 per cent. For when the solution of whatever concentration was carefully saturated with sodium chloride, a portion only of the substance separated out, while the residue was precipitated only upon the addition of acetic acid.

The latter portion, however, did not consist of deuteroalbumose as would at first appear, for after dialysis or neutralisation of the acetic

acid, it was then found precipitable by sodium chloride, although only partially so, a portion still remaining precipitable only on the addition of acid; the same process continually repeated with this latter portion until the material was entirely used up always led to the same result. The portion precipitated by sodium chloride alone also behaved in the same peculiar manner, being only partially separated from its solution on the second, third and fourth times, etc., by excess of sodium chloride, a portion of what appeared to be deutoalbumose remaining dissolved each time, and not differing in its properties from that obtained in the first series of experiments.

The first view which quite naturally suggested itself here, viz. that protalbumose by the method of treatment passes over into deutoalbumose and *vice versa*, is untenable, since we found the latter body prepared by a somewhat different process from different material, not at all precipitable by excess of sodium chloride alone. Deutoalbumose, therefore, remains characterised by its exclusive precipitation with salt and acid, while to protalbumose is to be ascribed the peculiarity of being only partially precipitated by sodium chloride, a residue remaining each time which requires the presence of acid for its separation.

The further properties of the four varieties of albumose we have studied in the above preparations, prepared from fibrin by pepsin-hydrochloric acid, and later from such preparations as were obtained from commercial material. As, however, no difference was found in the two series of preparations, the following detailed description will answer for the products in each case.

Preparation of the four kinds of albumose from Witte's so-called peptone.

The commercial preparation manufactured in Rostock by Fr. Witte might be made to render great service to the chemistry of digestion, and to this end the unfortunately quite erroneous name of the product needs to be changed to one more strictly descriptive of its nature. The preparation, as is well known to many, contains hardly any peptone, and so long as it is known by that name in the trade this fact cannot but reflect against it. In every other respect we feel compelled to acknowledge our indebtedness to the preparation, in the use of which we had no hesitation, since the

manufacturer of his own accord and in the most friendly manner confided to one of us the secret of the method of preparation. We have found it to contain nothing other than the products naturally to be expected in the immediate solution of well-washed raw fibrin in pepsin digestive mixture, and have found it much preferable to the large quantities of fluid necessarily obtained, and by which our work had hitherto been impeded.¹

500 grams of the light, white powder were rubbed up with 1500 grams of sodium chloride, whereby the dust immediately disappeared, as the mass became somewhat moist and gummy. To this we added, with vigorous stirring and trituration, 5 litres of water, after which a large piece of rock salt was so placed that it lay on the surface of the mixture. On the next day all that had separated was collected upon a cloth filter and placed under a press. The coarse, almost dry powder was then rubbed up with a large quantity of saturated salt solution, washed and again pressed. Although only slightly moist, the mass weighed almost 500 grams; it was placed in 6 litres of water, after 24 hours clarified by filtration through cloth, precipitated a second time with sodium chloride, of which 1800 grams were added in order to accomplish the saturation. This precipitate, again washed with saturated salt solution and pressed, dissolved almost completely in 2 litres of water, as did also the substance precipitated a third time with sodium chloride. The solution finally obtained was distributed in a large number of dialysing tubes and dialysed in running water until no chlorine reaction could be obtained. In order to prevent precipitation of the albumose in the latter reaction, either by nitric acid alone, or as a silver precipitate, it is necessary to add an excess of nitric acid, or else acetic acid, both to the albumose and silver solution.

During the dialysis numerous lumps of heteroalbumose separated in the tubes, and a gummy layer of the same body was smeared over the entire inner surface of the parchment, which latter could be obtained only by cutting open the tube and scraping it with a spatula.

I. *Protalbumose.*

From the clear aqueous solution, which like all albuminous solutions reacted noticeably alkaline, protalbumose was separated

¹ Witte's "pepton" was likewise recommended for the same purpose by Salkowski, who had recognised the preparation as a mixture of hemialbumose and peptone. Compare Salkowski and Leube, *die Lehre vom Harn*, 1882, 211.

for the fourth time by salt, again dissolved in water, whereby nothing remained undissolved other than a small amount of gypsum coming from the rock salt, and dialysed, this time with no sign of a turbidity.

During purification the quantity continually and rapidly diminished in favor of a portion always precipitable from the salt saturated filtrate by acetic acid. So in a like manner the final purified product, four times precipitated, was only partially, about half, precipitable by sodium chloride alone. Trituration of the dry substance with solid sodium chloride and then pouring on saturated salt solution likewise failed to produce a complete precipitation, even with a great increase of the absolute quantity of sodium chloride. This latter point is worthy of notice, since frequently a precipitation is obtained in the clear filtrate by the addition of a saturated salt solution alone, in cases where, in spite of the previous saturation of the fluid, there was not enough salt present in proportion to the organic substance. However, none of the substance precipitable by acetic acid from the filtrates of the second to the fourth sodium chloride precipitates agreed with deutoalbumose, since the solution of each of these precipitates produced after acidifying, were again precipitated by sodium chloride alone, although as before only partially.

Protalbumose was precipitated from the aqueous solution either directly with alcohol, or to economise the alcohol, after concentration. At first fearing alteration of the substance by heat, we carried on the evaporation of the solution at 40° C. (naturally with addition of thymol); but as it soon became apparent that no visible change took place even by boiling, the solutions were finally concentrated on the water-bath.

After precipitation with alcohol, washing with absolute alcohol and finally with ether, protalbumose dries quickly to a snow-white mass, even when in large lumps. It does not dissolve very rapidly in water, but still so abundantly that it is possible to obtain even syrupy solutions. The solutions are colorless, not quite clear, although nearly transparent, and always very slightly alkaline; in which connection it is worth noticing that Witte's preparation reacted faintly acid, and when dissolved in water with a trace of alkali was a little turbid.¹ Exact neutralisation of the

¹ Portions obtained from the manufacturer later were in several cases faintly alkaline.

protalbumose did not change the appearance or behavior of the solution.

The aqueous solution does not become clear at once on the addition of acid, but does finally in the presence of a certain excess of acetic acid; boiling does not affect it even in the presence of a small or great excess of acid; made slightly acid it is not rendered turbid by a little sodium chloride; on the addition of more salt it becomes opalescent, which passes away on the slightest warming, returns by cooling, even when the solution was previously boiled. If sufficient sodium chloride is added to produce in the cold a moderate precipitate, it is at once dissolved to a clear solution by boiling, but reappears as the solution cools. Finally, it is possible to add an amount of sodium chloride in the presence of which the acidified solution will no longer become clear by boiling.

Addition of a few drops of pure nitric acid to a solution of protalbumose free from salt produces a white precipitate, which on shaking is completely redissolved and then is reprecipitated by each new drop of acid added. In this manner it is possible to reach a point when after agitating the solution only a slight turbidity remains, which disappears by warming the solution very gently and again returns on cooling. This relatively small amount of acid is sufficient to produce a faint red (not yellow) color. More nitric acid dissolves the precipitate in the cold with formation of a yellow color; only sodium chloride will produce a precipitate now; the precipitate, however, is completely dissolved by heat, but reappears on cooling.

An aqueous solution of protalbumose strongly acidified with acetic acid is rendered quite turbid by a little potassium ferrocyanide, the precipitate not being dissolved when heated. If the quantity of acetic acid is increased a much larger amount of potassium ferrocyanide is needed to produce a precipitate. It is possible, however, to have the proportion of acid and ferrocyanide such that the mixture appears quite turbid in the cold, but when boiled becomes quite clear, growing turbid again as the solution cools. We have also repeatedly noticed in studying these different forms of albumose, that when mixed in certain proportions the potassium ferrocyanide precipitates are dissolved by a little acetic acid in the cold. These reactions are, however, somewhat uncertain, as the mixtures sooner or later become green or blue from decomposition of the salt.

Sodium hydroxide renders solutions of protalbumose quite clear at first, but when present in excess it causes a turbidity and even produces a precipitate. Solutions which have stood for some time with sodium hydroxide or with dilute hydrochloric acid, or which have been boiled with acetic acid, are not precipitated by neutralisation.

Solution of the substance, saturated with sodium chloride and filtered, is rendered only slightly turbid by boiling and does not become more so when cold. The smallest quantity of acetic acid then produces a heavy turbidity, even at 100°C . Excess of glacial acetic acid renders the fluid perfectly clear, which on being cooled after boiling deposits only crystals of salt. Nitric acid produces the same appearances in the fluid saturated with salt as in solutions free from salt (!).

Of the metallic salts, cupric sulphate, mercuric chloride and basic lead acetate produce heavy precipitates; the first and last, in contradistinction to the mercuric chloride precipitate, being soluble in excess of the reagent; all three of the precipitates, however, appear not to be even partially soluble on heating. Neutral lead acetate added to a faintly acid solution of protalbumose fails to produce any precipitate whatever, but the first few drops added to a really alkaline solution produce a precipitate which, however, is redissolved by an excess of lead.

With sodium hydroxide and a little dilute cupric sulphate a beautiful reddish violet color is produced. By boiling with lead acetate and an alkali hydroxide a deep blackening of the solution occurs, from the formation of lead sulphide.

We found the same reactions to be good also for that portion of the protalbumose not precipitated by sodium chloride alone. This portion was prepared by adding acetic acid to the filtrate saturated with salt, dissolving the precipitate in water, neutralising, dialysing, evaporating at 40°C ., and finally precipitating with alcohol. Both portions of protalbumose were found to be not completely precipitated by trituration with excess of magnesium sulphate nor by saturation with sodium sulphate and sodium chloride, as the filtrates in each case saturated with the salts were still precipitated by acetic acid.

In determining the composition of protalbumose five different preparations were employed:

- A*, purified by being four times precipitated;
- B*, purified by three precipitations;

C, prepared directly from an artificial digestion of fibrin, purified by two precipitations;

D, prepared from the same material as *C*, being the first portion precipitated by sodium chloride alone;

E, obtained in the same manner as *C* and *D*, being the second portion, precipitated by acetic acid after saturation with salt.

With the exception of *A*, which contained a trace of chlorine, all of the preparations were found, when tested both in concentrated solutions and after ignition, to be entirely free from chlorine. The content of ash was variable, in some cases being very small, and depended exclusively or at least in great part on the amount of calcium sulphate contained in the rock salt; after making the sulphur determinations the sulphur of the ash was deducted. Carbonate was present in the ash only once and then only in traces. The method of analysis was similar to that employed previously;¹ the substance in the form of a fine powder was dried at 105° C. *in vacuo*, carbon and hydrogen were determined by burning with cupric oxide, lead chromate and a roll of metallic copper in oxygen gas, nitrogen was determined as gas by burning with cupric oxide and a layer of metallic copper in a tube exhausted by a Sprengel pump, the sulphur by fusion with potassium hydroxide and nitrate and precipitation as barium sulphate.

A.

I. 0.4864 gram gave 0.2985 gram H₂O = 6.81 per cent. H and 0.9009 gram CO₂ = 50.50 per cent. C.

II. 0.4594 gram gave 0.2790 gram H₂O = 6.75 per cent. H and 0.8487 gram CO₂ = 50.38 per cent. C.

III. 0.6136 gram gave 89.63 cc. N at 23° C. and 760.45 mm. pressure = 0.1038901 gram N = 16.93 per cent.

IV. 0.4430 gram gave 63.96 cc. N at 21.6° C. and 766.5 mm. pressure = 0.0750823 gram N = 16.94 per cent.

V. 0.4720 gram gave 68.76 cc. N at 22.8° C. and 767 mm. pressure = 0.0804362 gram N = 17.04 per cent.

VI. 0.6234 gram gave 0.0055 gram ash = 0.89 per cent.

VII. 0.5206 gram gave 0.0048 gram ash = 0.92 per cent.

The ash consisted mainly of calcium sulphate and was free from carbonate; the ash from 1.1440 grams substance dissolved in dilute

¹ Compare Zeitschrift für Biologie, 19, 166.

IX. 0.5130 gram gave, after the fusion, 0.3483 gram $\text{BaSO}_4 = 1.29$ per cent. S; deducting 0.10 per cent. = 1.19 per cent. S.

	C	H	N	S	O	Average.
50.95	50.83	50.89
6.87	6.80	6.83
...	..	17.08	17.09	17.18	...	17.12
...	1.14	1.20
...	23.99

B.

IX. 0.6170 gram gave 0.0521 gram $\text{BaSO}_4 = 1.15$ per cent. S; deducting 0.03 per cent. = 1.12 per cent. S.

	C	H	N	S	O	Average.
50.35	50.35	50.48	50.39
6.78	6.70	6.73	6.74
...	17.20	17.04	...	17.12
...	1.03	1.07
...	24.68

C.

I. 0.7103 gram gave 0.4176 gram H_2O = 6.53 per cent. H and 1.2808 grams CO_2 = 49.17 per cent. C.

II. 0.6136 gram gave 0.3600 gram H_2O = 6.51 per cent. H and 1.1097 grams CO_2 = 49.31 per cent. C.

III. 0.3551 gram gave 0.2088 gram H_2O = 6.53 per cent. H and 0.6411 gram CO_2 = 49.23 per cent. C.

IV. 0.6507 gram gave 94.38 cc. N at 20° C. and 757.33 mm. pressure = 0.1100642 gram N = 16.91 per cent.

V. 0.5481 gram gave 78.82 cc. N at 19.2° C. and 761.45 mm. pressure = 0.0926730 gram N = 16.90 per cent.

VI. 0.5407 gram gave 0.0138 gram ash = 2.55 per cent.

VII. 0.6306 gram gave 0.0165 gram ash = 2.61 per cent.

The ash was composed of calcium sulphate, with a trace of calcium phosphate without any carbonate.

The ash from 1.1713 grams substance gave 0.0427 gram BaSO_4 = 0.50 per cent. S contained in the ash of the original substance.

VIII. 0.6163 gram gave after fusion with the nitrate 0.0705 gram BaSO_4 = 1.57 per cent. S; deducting 0.50 per cent. as coming from the ash = 1.07 per cent. S.

IX. 0.5373 gram gave 0.0664 gram BaSO_4 = 1.69 per cent. S; deducting 0.50 per cent. = 1.19 per cent. S.

Percentage composition of ash-free protalbumose C:

								Average.
C	50.47	50.62	50.53	50.54
H	6.70	6.68	6.70	6.69
N	17.35	17.34	17.34
S	1.11	1.23	1.17
O	24.26

D.

I. 0.6067 gram gave 0.3686 gram H_2O = 6.75 per cent. H and 1.1323 grams CO_2 = 50.89 per cent. C.

II. 0.5643 gram gave 0.3403 gram H_2O = 6.70 per cent. H and 1.0567 grams CO_2 = 51.06 per cent. C.

III. 0.6055 gram gave 0.3676 gram H_2O = 6.74 per cent. H and 1.1315 grams CO_2 = 50.95 per cent. C.

IV. 0.6757 gram gave 97.98 cc. N at 19.8° C. and 760.38 mm. pressure = 0.1148016 gram N = 16.98 per cent.

V. 0.6348 gram gave 90.28 cc. N at 18.3° C. and 768.66 mm. pressure = 0.1074839 gram N = 16.93 per cent.

VI. 0.6609 gram gave 0.0070 gram ash = 1.05 per cent.

VII. 1.1512 grams gave 0.0124 gram ash = 1.07 per cent.

The ash contained no carbonate, only calcium sulphate.

The ash from 1.8121 grams substance gave 0.0175 gram BaSO_4 = 0.13 per cent. S, calculated on the original substance.

VIII. 0.6650 gram gave after the nitrate fusion 0.0525 gram BaSO_4 = 1.08 per cent. S; deducting the 0.13 per cent. S of the ash = 0.95 per cent.

IX. 0.5643 gram gave 0.0425 gram BaSO_4 = 1.03 per cent. S; deducting 0.13 per cent. = 0.90 per cent. S.

Percentage composition of the ash-free protalbumose *D*:

								Average.
C	51.43	51.60	51.49	51.50
H	6.82	6.77	6.81	6.80
N	17.16	17.11	17.13
S	0.96	0.91	0.94
O	23.63

E.

I. 0.3993 gram gave 0.2445 gram H_2O = 6.80 per cent. H and 0.7329 gram CO_2 = 50.05 per cent. C.

II. 0.5722 gram gave 0.3452 gram H_2O = 6.70 per cent. H and 1.0437 grams CO_2 = 49.74 per cent. C.

III. 0.7986 gram gave 0.4890 gram H_2O = 6.80 per cent. H and 1.4610 grams CO_2 = 49.88 per cent. C.

IV. 0.4635 gram gave 66.16 cc. N at 19.8° C. and 763.4 mm. pressure = 0.0778265 gram N = 16.79 per cent.

V. 0.5845 gram gave 83.56 cc. N at 19.6° C. and 761.26 mm. pressure = 0.0980867 gram N = 16.78 per cent.

VI. 0.8561 gram gave 0.0115 gram ash = 1.34 per cent.

VII. 0.6389 gram gave 0.0083 gram ash = 1.30 per cent.

The ash contained no carbonic acid, only calcium sulphate and a trace of phosphate.

The ash from 1.4950 grams substance gave 0.0091 gram BaSO_4 = 0.08 per cent. S, calculated on the original substance.

VIII. 0.5187 gram gave in the nitrate fusion 0.0426 gram BaSO_4 = 1.12 per cent. S; deducting 0.08 per cent. as coming from the calcium sulphate of the ash = 1.04 per cent. S.

IX. 0.7779 gram gave by fusion 0.0642 gram BaSO_4 = 1.13 per cent. S; deducting 0.08 per cent. = 1.05 per cent. S.

Percentage composition of the ash-free protalbumose *E*:

								Average.
C	50.71	50.40	50.55	50.55
H	6.89	6.78	6.89	6.85
N	17.01	17.00	17.01
S	1.06	1.07	1.07
O	24.52

The analyses show such close agreement it is evident that the five preparations cannot be considered as bodies of noticeably different percentage composition. The very slight differences vary on an average in such a manner that, while the nitrogen (the values of which are naturally to be considered as somewhat high) shows hardly any variation, lower percentages of carbon answer to higher percentages of hydrogen, so that the slight differences are without doubt due to small fluctuations in the content of water. In this manner the two products obtained from *C*, viz. *D* and *E*, can be distinguished, the acetic acid precipitate (*E*) being considered as the hydrate.

As special value has of late been laid upon the specific rotary power of the different albumins and their digestive products, an attempt was made to determine these physical characters of the several specimens of protalbumose. Unfortunately we were not able to carry out the observations in as exact a manner as seemed to us desirable, since concentrated solutions were as a rule too turbid for use; and even in the more dilute solutions it was necessary, in making an observation with a tube 200 millimetres long, to clarify the solution with a little hydrochloric acid, which might possibly alter its rotary power, in order to render it sufficiently transparent. The determinations were made by means of a large Wild's polaristrobometer with sodium light. They led to the following results:

Protalbumose A.

0.7986 gram substance dried at 105° C. *in vacuo* = 0.7915 gram ash-free substance dissolved in 40 cc. H₂O + 10 cc. 0.2 per cent. HCl, rotated the plane of light 2.3° to the left as an average of 3 determinations in a 200 mm. tube. Therefore, with 0.015883 gram of pure substance in 1 cc.,

$$(\alpha)_D = \frac{2.3^\circ}{0.015883 \cdot 2} = -72.64^\circ.$$

Protalbumose B.

1.1411 grams dried in the same manner as *A* = 1.1386 gram ash-free substance dissolved in 40 cc. H_2O + 10 cc. 0.2 per cent. HCl rotated the plane of light as a mean of 5 observations 3.6° to the left; thus, with 0.02277 gram pure substance in 1 cc.,

$$(\alpha)_D = \frac{3.6^\circ}{0.02277 \cdot 2} = -79.05^\circ.$$

Protalbumose C.

0.9881 gram dry = 0.9627 gram ash-free substance dissolved in 30 cc. H_2O + 20 cc. 0.2 per cent. HCl ; rotation as a mean of 4 observations 3.0° to the left. With 0.019254 gram pure substance in 1 cc.,

$$(\alpha)_D = \frac{3.0^\circ}{0.019254 \cdot 2} = -77.90^\circ.$$

Protalbumose D.

0.6905 gram dry = 0.6832 gram ash-free substance dissolved in 35 cc. H_2O + 15 cc. 0.2 per cent. HCl ; rotation as a mean of 3 observations 2.0° to the left. With 0.013664 gram pure substance per cubic centimetre,

$$(\alpha)_D = \frac{2.0^\circ}{0.013664 \cdot 2} = -73.18^\circ.$$

Protalbumose E.

0.8515 gram dry = 0.8403 gram ash-free substance dissolved in 30 cc. H_2O + 20 cc. 0.2 per cent. HCl ; rotation as a mean of 4 observations 2.4° to the left. Therefore, with 0.016806 gram pure substance per cubic centimetre,

$$(\alpha)_D = \frac{2.4^\circ}{0.01680 \cdot 2} = -71.40^\circ.$$

The specific rotary power certainly varies in these preparations to a not inconsiderable extent, the maximum variation being 7.65° ; we are, however, of the opinion that in order to draw any conclusion from these determinations, more exact studies of the influence of the solvent used in rendering the solutions transparent are necessary.

II. *Deuteroalbumose.*

We have obtained this body in the purest condition from Witte's albumose. The method of separation consisted in the addition of acetic acid to the filtrate (to which the salt solution used in washing the protalbumose had not been added) from the first salt-albumose precipitate. It was an easy matter to collect the precipitate formed in this manner on a cloth filter, and after thorough washing with saturated salt solution the mass was found to be so pure that it needed only one more precipitation with salt and acid. On dialysis the substance parted with the last portions of acid quite slowly; it therefore seemed desirable after the removal of the greater portion of the acid to neutralise carefully with sodium hydroxide, so that at the last only the acetate remained for further dialysis. In no case was a turbidity noticed either on neutralisation or after removal of the acetic acid by dialysis,¹ by which, however, the solution became noticeably alkaline. On the other hand it was occasionally necessary to remove from the neutralised fluid a deposit of heteroalbumose which had separated during dialysis.

From the thoroughly dialysed solution deuteroalbumose was obtained by evaporation, precipitation with alcohol, washing with absolute alcohol and ether, as a white, light powder, which aside from a slight admixture of gypsum (0.68-1.77 per cent.) was apparently quite pure. A solution of the substance could be concentrated on a water-bath without suffering any noticeable change. Following are the general characters of the body.

It is not precipitated by saturation with sodium chloride; after standing days and even weeks with an excess of clean salt crystals the solution remained perfectly clear, and after filtration and washing with saturated salt solution nothing remained upon the filter which would give to suitable solvents anything colored yellow by nitric acid. By boiling the solution saturated with sodium chloride

¹ This removal of the acid by dialysis succeeds with many of the albuminous bodies; a solution of flesh-(myosin-)syntonin, for example, in HCl of from 0.1-0.5 per cent. with or without the addition of thymol is in this manner completely precipitated neutral and free from chlorine; in a similar manner a digestive mixture with pepsin-HCl will deposit not only the whole of the so-called neutralisation precipitate, but also hetero- and dysalbumose. With the various forms of albumose, however, complete removal of the acid by dialysis is less to be recommended, since these bodies though difficultly diffusible, pass through parchment much more rapidly than the original albumin, and thus the loss by long-continued dialysis becomes quite appreciable. On the other hand dialysis is peculiarly adapted to the precipitation of myosin-salt solutions, which as is well known require for their precipitation with water the addition of very large quantities and at the same time give a too finely divided precipitate. In the dialyser, however, the volume of fluid is but little increased, while the precipitate which forms is very compact and does not become difficultly soluble in salt solutions of suitable strength.

no special precipitation is to be seen, but the fluid resembles a frothy jelly filled with bubbles, which appearance disappears on cooling, or at the most in place of the shrunken froth is to be seen only a few short white shreds or fibres.

A solution of deuteroalbumose free from salt, made by dissolving some of the pure substance in cold, distilled water, is not altered by boiling and cooling, not even after acidifying slightly with acetic acid; by nitric acid in any proportion and at any temperature the solution is not rendered turbid, though a slight excess of acid produces a yellow color even in the cold. If the yellow solution is mixed with sufficient sodium chloride to produce a strong turbidity and then warmed, the solution becomes perfectly clear long before the boiling point is reached, but as the solution cools the turbidity reappears. The same reactions appear when a little sodium chloride is added before acidifying. Solution of the albumose made faintly acid with acetic acid and then mixed with a few drops of sodium chloride solution can remain perfectly clear; as the solution is gently warmed a turbidity appears, which by stronger heat entirely passes away, the solution becoming once more clear; then on cooling a permanent turbidity makes its appearance, which, however, can be made to disappear by heating the solution nearly to boiling. On the addition of more sodium chloride a point is reached where the moderate-sized precipitate formed is entirely dissipated by heat, reappearing as the solution cools; and then again there is another proportion where a slight turbidity remains on boiling, and finally still another where an apparently constant precipitate is formed at 100° C. If now the latter mixture is filtered hot, the solution at first passes through the paper perfectly clear, but on cooling a decided turbidity appears. This also happened when solid sodium chloride had been added to saturation, equally as well whether the amount of acid present was small or quite large. In the latter case the clear fluid filtered from the precipitate which formed prior to the heating gives by moderate warming a precipitate which disappears by stronger heat, remaining clear even when the solution becomes cold. If an excess of either ordinary or glacial acetic acid saturated with salt be added to a salt-saturated solution of deuteroalbumose, the precipitate is completely dissolved even in the cold; boiling and then cooling the solution has no effect on it whatever.

Towards acetic acid and potassium ferrocyanide deuteroalbumose behaves in all respects exactly like protalbumose, also towards

	C	H	N	S	O	Average.
50.43	50.46	50.51	50.47
6.69	6.91	6.83	6.81
...	17.13	17.30	17.17	17.20
...	0.85	0.87
...	24.65

Deuteroalbumose G.

I. 0.4631 gram gave 0.2865 gram H_2O = 6.87 per cent. H and 0.8603 gram CO_2 = 50.66 per cent. C.

II. 0.5730 gram gave 0.3500 gram H_2O = 6.78 per cent. H and 1.0598 grams CO_2 = 50.43 per cent. C.

III. 0.5302 gram gave 0.3228 gram H_2O = 6.76 per cent. H and 0.9800 gram CO_2 = 50.40 per cent. C.

IV. 0.4824 gram gave 70.15 cc. N at 21.2° C. and 765.14 mm. pressure = 0.0823142 gram N = 17.06 per cent.

V. 0.5630 gram gave 81.07 cc. N at 20.6° C. and 766.65 mm. pressure = 0.0955107 gram N = 17.00 per cent.

VI. 0.6434 gram gave 0.0046 gram ash = 0.70 per cent.

VII. 0.7275 gram gave 0.0048 gram ash = 0.66 per cent.

The ash contained no carbonic acid, but consisted wholly of calcium sulphate.

The ash from 1.3709 grams substance gave 0.0059 gram $BaSO_4$ = 0.06 per cent. S, calculated on the original substance.

VIII. 0.7779 gram substance gave by the nitrate fusion 0.0639 gram $BaSO_4$ = 1.12 per cent. S; deducting 0.06 per cent. = 1.06 per cent. S.

IX. 0.5180 gram gave by the nitrate fusion 0.0425 gram $BaSO_4$ = 1.12 per cent. S; deducting 0.06 per cent. = 1.06 per cent. S.

Percentage composition of ash-free deuteroalbumose *G*:

								Average.
C	51.00	50.77	50.75	50.84
H	6.92	6.83	6.81	6.85
N	17.17	17.11	17.14
S	1.07	1.07	1.07
O	24.10

Examination of the specific rotary power gave the following results:

Deuteroalbumose *F*: 0.8550 gram dry substance = 0.8399 gram ash-free substance dissolved in 35 cc. H_2O + 15 cc. 0.2 per cent. HCl rotated the light 2.5° to the left, as a mean of 4 observations in a 200 mm. tube, hence with 0.016798 gram pure substance per cubic centimetre,

$$(\alpha)_D = \frac{2.5^\circ}{0.016798 \cdot 2} = -74.41^\circ.$$

Deuteroalbumose *G*: 0.7635 gram dry = 0.7584 gram ash-free substance dissolved in 40 cc. H_2O + 10 cc. 0.2 per cent. HCl

rotated the light as a mean of 4 observations 2.4° to the left; thus with 0.015168 gram pure substance in 1 cc.,

$$(\alpha)_D = \frac{2.4^{\circ}}{0.015168 \cdot 2} = -79.11^{\circ}.$$

Deuteroalbumose does not therefore differ essentially either in composition or in its optical properties from protalbumose; both are to be considered on like grounds as the first hydrates of albumin.

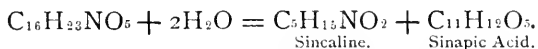
(To be continued.)

INVESTIGATIONS ON SINAPINE.

I.—ON SINAPIC ACID.

BY IRA REMSEN AND R. D. COALE.

In the year 1825 Henry and Garot¹ discovered a new substance in white mustard seed, and to it they gave the name *sulpho-sinapic acid*. In 1852 von Babo and Hirschbrunn² published the results of an elaborate investigation of this substance, since which time practically nothing has been added to our knowledge of the subject. What is at present known may be briefly summed up. The substance which can be extracted from mustard seed by alcohol is the sulphocyanate of a base known as sinapine. The base has the composition represented by the formula $C_{16}H_{23}NO_5$, the sulphocyanate being $C_{17}H_{24}N_2SO_5$. When the base is boiled with an alkali it undergoes decomposition, yielding two products, *sinapic acid* and *sincaline*, a new base. The decomposition is represented by the equation:



Claus and Keesé³ have examined sincaline, and have made it appear extremely probable that this base is identical with the substance known as choline, bilineurine and trimethylethoxy-

¹ Journ. Pharm., **17**, 1; **20**, 63.

² Annalen der Chemie, **84**, 10.

³ Zeitschrift für Chemie, 1868, 46.

ammonium hydroxide $(\text{CH}_3)_3\text{N}(\text{C}_2\text{H}_5\text{O}).\text{OH}$. Satisfactory proofs of the identity have, however, not been furnished.

As regards sinapic acid the only facts established by von Babo and Hirschbrunn are the composition, represented by the formula $\text{C}_{11}\text{H}_{12}\text{O}_5$, the instability of its salts and the composition of a barium salt, $\text{C}_{11}\text{H}_{10}\text{O}_5\text{Ba}$. After giving the results of the analyses of this salt von Babo says: "Da es nicht leicht ist, ein anderes Salz der Säure in zur Analyse geeignetem Zustand zu erhalten und ich nicht zu viel Material diesen Versuchen opfern konnte, musste die Entscheidung der Frage, ob die Säure ein- oder zweibasisch ist, für jetzt unterbleiben." As the salt was prepared by treating the acid with an excess of baryta water, the fact that it has the composition $\text{C}_{11}\text{H}_{10}\text{O}_5\text{Ba}$ might indicate that the acid is bibasic, or that it contains phenol hydroxyls, or, finally, one hydroxyl and one carboxyl. According to the formula above given it has the composition of a propyl ether of one of the hydroxy-phthalic acids, $\text{C}_6\text{H}_3 \begin{cases} \text{OC}_3\text{H}_7 \\ (\text{COOH})_2 \end{cases} = \text{C}_{11}\text{H}_{12}\text{O}_5$. This fact awakened our interest in the acid, as the researches of one of us during the past few years have had more or less connection with the hydroxy-phthalic acids. We have hence undertaken a new investigation of sinapine and its decomposition products, and in this paper will communicate the results reached in connection with sinapic acid, leaving for a future communication the subject of sincaline. Various circumstances have tended to delay the progress of the investigation, and even now the results are not all that we could wish for. As we have, however, succeeded in throwing considerable light upon the nature of sinapic acid, and have indeed reached a definite conclusion concerning its constitution, we give here the results already obtained, hoping soon to be able to conclude the investigation.

Preparation of Sulphocyanate of Sinapine.

According to von Babo and Hirschbrunn the maximum yield of the sulphocyanate obtainable is 0.5 gram from a pound of white mustard seed. In order to obtain a sufficient quantity to work with satisfactorily, it was hence necessary to start with a large quantity of mustard seed. We had 100 pounds of unground white mustard seed thoroughly pressed, to free it from oil, and then placed the pressed seed in the hands of a manufacturing chemist who kindly undertook for us the work of extraction. This was

accomplished as follows: The seed was digested in portions of 10 pounds each with four to five gallons of 95 per cent. alcohol. About one gallon of the alcohol remained in each portion and could not be recovered by filtration and pressure. The combined alcoholic extracts were evaporated until one gallon of the residue represented 10 pounds of the seed. This concentrated extract was delivered to us and formed the starting point of our work. It was further concentrated by distillation to about one-fifth its volume and divided into four equal portions of two to three litres each. To one of these portions a small quantity of an alcoholic solution of potassium sulphocyanate was added, and after a few days this portion was found to be filled with a mass of feathery crystals, while the other portions were free from the deposit. These were therefore also treated with an alcoholic solution of potassium sulphocyanate, and in a few days the crystals appeared in them as in the first portion. The crystals were filtered off through cotton cloth, pressed carefully and then recrystallised from water. The alcoholic mother-liquors were placed aside, and, after standing for some days, crystals were again deposited from them. From time to time these successive deposits were filtered off, pressed and recrystallised, and were thus easily obtained in pure condition. Two crystallisations from water were usually quite sufficient to thoroughly purify the substance. We obtained in all about 80 grams of the pure substance from 100 pounds of the seed, a somewhat better yield than that obtained by von Babo and Hirschbrunn, which, as stated above, was only 0.5 gram from a pound of mustard seed. These chemists seem to have had much more difficulty in getting the crystals out of their extracts than we had. They recommend that the extracts be distilled until the greater part of the alcohol has passed over, and the residue on cooling separates into two layers about equal in size, one of oil and the other of the solution of sinapine sulphocyanate. They say that the entire success of the operation depends upon hitting exactly the right concentration of the liquid. If the evaporation is not carried far enough a great deal of sinapine remains in the oil. If, on the other hand, the evaporation is carried too far, the sinapine undergoes decomposition, or products are formed which prevent its crystallisation. At first we tried faithfully to hit the proper concentration at which the liquid should separate into two layers. After a great many efforts we finally gave this up, and worked as above described, and with entirely satisfactory results. The use of

a centrifugal machine for the purpose of freeing the crystals from the thick mother-liquor we have also found unnecessary. Although the first deposit contained indeed some gummy matter, and its filtration was not effected as easily as that of the succeeding portions, still it was easily purified by crystallising from water, in which the gummy matter appeared to be entirely insoluble. The purification by crystallisation from water appears to be much more satisfactory than that from alcohol, as recommended by von Babo and Hirschbrunn.

The sulphocyanate of sinapine obtained as above described crystallises from water in beautiful, feathery crystalline masses. It is nearly colorless, though repeated crystallisations failed to remove a slight yellowish tint. It is difficultly soluble in cold water, easily in hot. It melts at 176° , not at 130° as stated by von Babo and Hirschbrunn. In other respects the properties of our product agree perfectly with those given by these authors.

Preparation of Sinapic Acid from Sinapine Sulphocyanate.

Von Babo and Hirschbrunn effected the decomposition of sinapine into sincaline and sinapic acid by boiling with caustic potash. On then adding hydrochloric acid, the acid was thrown down. In preparing sincaline, however, they used baryta water, thus obtaining the acid in the form of an insoluble, stable barium salt. We have found that for the purpose of preparing the acid the decomposition of the sinapine is best effected by means of baryta water. Our process is as follows: 20 grams barium hydroxide are dissolved in 300 cc. water and 10 grams of the sulphocyanate of sinapine added. The solution turns markedly yellow, and a yellow precipitate is formed. The mixture is boiled for a few minutes to complete the decomposition, and the precipitate then filtered off. It is washed with water, brought into a flask and treated with dilute hydrochloric acid. The sinapic acid is thus obtained in the form of a dirty white precipitate. It is crystallised from water, the quantity obtained in a single experiment being soluble in 500 cc. hot water. From the solution it is deposited in fine well-formed needles which have a slight yellow color. The yield from 10 grams sulphocyanate of sinapine is about 6 grams, the theoretical yield being but a small fraction more than 6 grams. On concentrating the mother-liquor it becomes dark colored, and on cooling deposits a reddish-brown gelatinous mass. This is at least partly

due to a slight decomposition of the acid by boiling with water alone, for the same thing was noticed when the purest acid was dissolved in water and the solution concentrated by boiling. This decomposition appears not to take place to as great an extent by boiling with alcohol or with alcohol and water. We have hence commonly employed a mixture of alcohol and water for the purpose of purifying it. The method finally adopted consisted in dissolving the acid in a small quantity of hot alcohol, then adding water until a precipitate was formed, heating gently until this dissolved, and then allowing to cool. The fusing points of different specimens vary. That which was crystallised from alcohol and water fused at 192° (corrected), and that from alcohol alone at 186.5° (corrected). The discoverers state that it melts "ohngefähr bei 150° bis 200° ."

The acid is difficultly soluble in cold water and cold alcohol, and easily soluble in the hot liquids. The crystals from the alcoholic solution are small transparent prisms, with a yellow color which could not be removed. Those from the aqueous solution are smaller. Both have the appearance of being perfectly homogeneous. As already mentioned, slight decomposition appears to take place more easily in the aqueous than in the alcoholic solutions. To determine whether this decomposition materially affected the composition of the substance, a number of combustions were made of products from various crystallisations. The first two analyses are of crystals obtained from water alone. The next two are of crystals obtained from alcohol and water—no special care being taken in regard to the time of boiling. The substance was dried at 130° before the analyses. The results obtained are here given:

I. 0.2988 gram substance gave 0.6399CO_2 ; and 0.1787 gram H_2O .

II. 0.2012 gram substance gave 0.4346CO_2 ; and 0.1124 gram H_2O .

III. 0.1998 gram substance gave 0.4333CO_2 ; and 0.1090 gram H_2O .

IV. 0.2015 gram substance gave 0.4370CO_2 ; and 0.1266 gram H_2O .

The substance used in the two next analyses was prepared in the same way as that used in the preceding ones, only, instead of being dried at 130° , it was dried by pressure between layers of bibulous paper and by standing in the air. The results are:

V. 0.2008 gram substance gave 0.4357 gram CO_2 ; and 0.1085 gram H_2O .

VI. 0.2008 gram substance gave 0.4367 gram CO_2 ; and 0.1073 gram H_2O .

The same substance was now recrystallised from alcohol and water, and dried in the air at the ordinary temperature. The results are:

VII. 0.2007 gram substance gave 0.4348 gram CO_2 ; and 0.1053 gram H_2O .

A new quantity of the acid was now prepared, and, in crystallising it, precautions were taken to perform the operation as rapidly as possible so as to reduce the risk of decomposition. It was crystallised from alcohol and water, and dried at 130° . The results of the analyses are:

VIII. 0.2003 gram substance gave 0.4302 gram CO_2 ; and 0.0921 gram H_2O .

IX. 0.2004 gram substance gave 0.4318 gram CO_2 ; and 0.1032 gram H_2O .

X. 0.2009 gram substance gave 0.4320 gram CO_2 ; and 0.1006 gram H_2O .

XI. 0.2495 gram substance gave 0.5376 gram CO_2 ; and 0.1258 gram H_2O .

A portion of the acid was now carefully crystallised from pure alcohol, and then dried at the ordinary temperature. The results obtained with this specimen are:

XII. 0.2010 gram substance gave 0.4308 gram CO_2 ; and 0.1011 gram H_2O .

XIII. 0.1958 gram substance gave 0.4173 gram CO_2 ; and 0.0964 gram H_2O .

XIV. 0.1628 gram substance gave 0.3522 gram CO_2 ; and 0.0817 gram H_2O .

The results of the first six analyses do not agree well with each other, as will be seen in the following table in which the percentages of carbon and hydrogen are given:

	I.	II.	III.	IV.	V.	VI.
C	58.41	58.91	59.15	59.15	59.18	59.31
H	6.64	6.21	6.06	6.98	6.00	5.94

The variation in composition shown by these analyses we believe to be due to slight decomposition of the acid caused by boiling with water and alcohol.

The results of the remaining eight analyses agree fairly well with each other and also with those obtained by von Babo and Hirschbrunn, from which these writers concluded that the formula of the acid is $C_{11}H_{12}O_5$.

	Calculated for $C_{11}H_{12}O_5$.	Found.					
		VII.	VIII.	IX.	X.	XI.	XII.
C	58.93	59.08	58.58	58.76	58.65	58.76	58.45
H	5.36	5.83	5.11	5.72	5.56	5.60	5.59
		v. B. and H.					
		XIII.		XIV.			
		58.13		59.00		58.67	58.92
		5.47		5.58		4.87	5.67

The first six analyses led us to the suspicion that the composition might be $C_{11}H_{14}O_5$ —with which formula the results of these analyses agree better than they do with the formula of von Babo and Hirschbrunn. In view of the results of the last eight, however, in which special precautions were taken to prevent decomposition, we think the evidence is overwhelming in favor of the original formula $C_{11}H_{12}O_5$.

Basicity of Sinapic Acid.

As above stated, von Babo and Hirschbrunn described and analysed a barium salt of sinapic acid, which was prepared by boiling the acid with an excess of baryta water. The composition of the salt as determined by them is represented by the formula $C_{11}H_{10}O_5Ba$, which requires 38.16 per cent. barium, while they found in two analyses 37.68 and 38.48 per cent. barium. This is the only salt analysed by them.

Our attempts to prepare crystallised salts were also unsuccessful. We nevertheless succeeded in analysing salts in solution, and in thus showing that the acid is really monobasic. For this purpose a weighed quantity of sinapic acid was brought into a flask with a small quantity of finely powdered Iceland spar, the mixture digested for some time on the water-bath, then boiled and filtered and the amount of calcium in the solution estimated.

0.2504 gram of the acid treated in the above manner gave 0.0329 gram CaO .

If the salt formed had been of the composition $C_{11}H_{10}O_5Ca$ the amount of calcium found would have been much greater, amounting to 15.27 per cent. of the total salt. The above weight of lime

corresponds, however, to only 8.65 per cent. calcium, assuming that the salt $(C_{11}H_{11}O_5)_2Ca$ has been formed; while this salt requires 8.23 per cent. calcium.

A similar result was obtained in an experiment with barium carbonate. 0.2005 gram of the acid was boiled with barium carbonate and water, filtered, and the amount of barium estimated by precipitating it as sulphate. The amount of sulphate found was 0.1144 gram. Assuming that the salt formed is $(C_{11}H_{11}O_5)_2Ba$, the sulphate found corresponds to 25.7 per cent. barium, while the salt requires 23.49 per cent. barium.

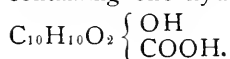
The salt described by von Babo and Hirschbrunn was also prepared and analysed by us. It was prepared directly from sinapine sulphocyanate by boiling with clear baryta-water, care being taken to prevent access of air. It was then thoroughly washed with boiling water to remove all traces of baryta water. After drying it gave the following results:

I. 0.2035 gram dried at 130° gave 0.1285 gram $BaSO_4$.

II. 0.1998 gram dried at 140° gave 0.1266 gram $BaSO_4$.

Calculated for. $(C_{11}H_{11}O_5)_2Ba$.		Found.	
		I.	II.
Ba	38.16	37.13	37.25

Although our results do not agree with the calculated percentage as well as those obtained by von Babo and Hirschbrunn, they nevertheless point to the same conclusion. From all the above results taken together it follows that sinapic acid is a monobasic acid containing one hydroxyl, a conclusion expressed by the formula



Action of Acetyl Chloride and Acetic Anhydride on Sinapic Acid.

When sinapic acid is boiled with acetyl chloride it dissolves partly, and crystallises out unchanged. Even prolonged boiling produces no change in the composition. Acetic anhydride, however, easily dissolves the acid when boiled, and, if water is added and the solution allowed to cool, a white crystallised compound separates. This is easily soluble in hot water, from which it was crystallised. It fuses at 281° . The analyses gave the following results:

I. 0.2008 gram gave 0.4336 gram CO_2 ; and 0.1067 gram H_2O .

II. 0.2007 gram gave 0.4318 gram CO_2 ; and 0.1047 gram H_2O .

	Calculated for $C_{10}H_{10}O_2 \begin{cases} O_2C_2H_3O \\ COOH \end{cases}$	Found.	
		I.	II.
C	58.65	58.89	58.68
H	5.26	5.91	5.80

This result confirms that obtained in working with the barium salts, and can leave little doubt that the acid contains one hydroxyl. It is clear from the above that sinapic acid is not a derivative of a hydroxy-phthalic acid.

Action of Potassium Hydroxide and other decomposing agents on Sinapic Acid.

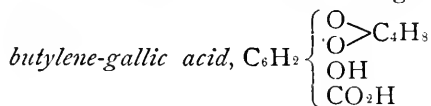
When sinapic acid is thrown upon fused caustic potash it turns green and gives off vapors which have the odor of ordinary incense. The same odor is noticed very strikingly when a little of the acid is heated on platinum foil. If the acid is stirred with the fused alkali it gradually enters into combination, forming a dark brown colored mixture. Prolonged heating is necessary to cause the disappearance of lumps of unchanged acid. The fused mass was allowed to cool, dissolved in water and immediately acidified with hydrochloric acid. A black, gelatinous precipitate was thrown down. This was filtered off and found to be soluble in alkalies, forming a dark-colored solution, from which it was again precipitated on the addition of hydrochloric acid. The small quantity of the precipitate obtained prevented any further investigation of it. The filtrate from this precipitate was extracted with ether, and on evaporation of the extract there remained a small quantity of a substance soluble in water, the solution turning dark with alkalies. With ferric chloride and ferrous sulphate the aqueous solution gave a black or dark green color. In a second fusion with caustic potash the heating was not continued as long as in the first experiment nor was the temperature raised as high. From the ethereal extract of this fusion there was obtained a very small quantity of a substance which gave the reactions of pyrogallol. With ferric chloride it gave a red color. With ferrous sulphate a dark blue. With milk of lime it gave a reddish tint which soon changed to a brown. The solution reduced nitrate of silver. Although, in this as well as subsequent experiments, we were unable to isolate enough of the product to make a satisfactory determination of the fusing point, we believe that the reactions are sufficient to show that the

product of the fusion of sinapic acid with caustic potash is pyrogallol. A number of efforts were made to effect a satisfactory decomposition by means of caustic potash, but they were not more successful than the one described.

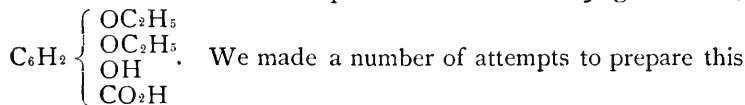
Taking the above facts into consideration, and recalling the properties of sinapic acid itself as established by von Babo and Hirschbrunn and confirmed by us, we can scarcely doubt that the acid is a derivative of gallic acid. The properties of the acid given by von Babo and Hirschbrunn more in detail than they have yet been stated, are as follows: The solution of the acid in caustic potash or soda changes very rapidly in the air. It passes through red to green and brown, and is transformed into other bodies. The ammonia salt turns reddish-brown. The precipitates with copper and lead salts are also rapidly changed, turning green or brown.

Thinking that possibly the decomposition of sinapic acid might be effected more perfectly by means of hydrochloric acid than by potassa, a small quantity was placed in a sealed tube with concentrated hydrochloric acid and then heated to 100° for $1\frac{1}{2}$ to 2 hours. The sinapic acid entirely disappeared, the hydrochloric acid became dark red, and a dark-colored gelatinous precipitate was floating in the solution. This was filtered off and found to resemble closely the black gelatinous precipitate obtained from the fusion with caustic potassa. No other substance could be separated. The experiment was repeated with the same result.

Assuming that sinapic acid is in reality a derivative of gallic acid, an assumption which seems fully justified by the facts, there is but one view to be taken in regard to its nature. It must be



At the beginning of our work we were for a time in doubt whether the composition of the acid is represented by the formula $C_{11}H_{12}O_5$ or $C_{11}H_{14}O_5$. Indeed the results of the first six analyses point rather to the latter formula as the correct one. We then further concluded that sinapic acid must be *diethyl-gallic acid*,



compound, but obtained nothing with exactly the properties of

sinapic acid. Finally we concluded to replace all the replaceable hydrogens of both sinapic and gallic acids with ethyl, hoping that thus we would in each case obtain the same final product, viz.: ethyl triethylgallate $C_6H_2 \begin{cases} (OC_2H_5)_3 \\ CO_2C_2H_5 \end{cases}$. In neither case, however, was a substance with characteristic properties obtained. The product was a dark-colored liquid which refused to solidify.

We propose to continue this investigation in the hope of effecting the synthesis of sinapic acid. The ethers of gallic acid can be made easily by starting from the lead compounds. For the purpose of comparison we shall attempt to make the methylene, ethylene, propylene and butylene ethers, and shall in due time communicate our results.

ON THE DETERMINATION OF NITROGEN BY COMBUSTION WITH CALCIUM HYDROXIDE.

(From the Annual Report of the Connecticut Agricultural Experiment Station for 1883, communicated by S. W. JOHNSON, Director.)

In a paper by the Director, published in the American Chemist for 1873 (vol. III, p. 161), it was shown that the mixture of sodium hydroxide and calcium hydroxide or oxide, proposed by Will and Varrentrapp as a reagent for converting organic nitrogen into ammonia for the purposes of analysis, may be advantageously replaced by a more easily prepared mixture of sodium carbonate and calcium hydroxide. When preparing that paper some combustions were made with simple calcium hydroxide; and in case of uric acid, for instance, the amount of nitrogen obtained fell short of the theoretical quantity by less than one per cent. As no entirely satisfactory results were then reached by burning with simple slaked lime, it was concluded that the presence of an alkali hydroxide, which it was thought might be formed in small quantity in the process of combustion, was necessary to the complete conversion of the nitrogen into ammonia. Further trials were then contemplated, but not until recently has the opportunity offered to carry them out. A series of analyses, whose results are here given,

demonstrate that this further simplification of the Will and Varrentrapp method applies to all those classes of substances which are ordinarily encountered in technical work.

The calcium hydroxide was prepared from a good quality of quicklime by slaking with water in but slight excess, drying off any surplus of water at a moderate heat, rubbing gently in a mortar, passing through a sieve of $\frac{1}{32}$ inch holes, and bottling in well-closed "fruit jars."

The tubes were filled and the combustions were made in the way indicated in the Report of the Connecticut Experiment Station for 1878, page 116. The points to be observed are chiefly these. For the burning of 0.5 gram of substances containing 8 per cent. of nitrogen or less, a tube of 14 inches is long enough. For dried blood or albuminoids containing from 12 to 17 per cent. of nitrogen a tube 2-4 inches longer is desirable.

The mixture of substance and slaked lime must not quite half fill the tube in lengthwise direction. The long anterior layer of slaked lime must be brought to a *full red heat* before heating the mixture, and must be so kept throughout the combustion.

No fumes or tarry matters, indicative of incomplete combustion, should appear in the bulb containing standard acid.

When the combustion proper is begun it may be carried on quite rapidly until completed.

The tube is cooled below a red heat before aspirating.

The ammonia from the combustion is received in standard hydrochloric acid and titrated with a standard ammonia solution, using tincture of cochineal as an indicator.

The advantages of using cochineal tincture instead of litmus solution are very considerable. It can be kept unaltered indefinitely, as litmus cannot; it is not seriously affected by the presence of carbonic acid in solutions, and as an indicator it is more sensitive.

In our use of the mixture of slaked lime and sodium carbonate, the acid in the bulb-tube is frequently colored more or less deeply red. This in nowise interferes with the alkalimetry, for the red color fades as the point of neutralisation is reached. In burning with simple slaked lime, the standard acid has almost invariably remained colorless, a fact which shows that the combustion with the latter is more perfect. It is evidently highly heated water vapor which at once oxidises the carbon and hydrogenises the nitrogen, and the slaked lime alone operates more effectually because it supplies more water in a given bulk of charge.

As was to be anticipated, the lime, at the full red heat to which it must be exposed, does not retain all the carbon dioxide that is formed; the gases which pass the standard acid give a copious precipitate in baryta-water. The standard acid, however, takes up from the heated gases too little carbon dioxide to sensibly affect the point of neutralisation, and the entire accuracy of the determination is in no degree impaired.

The contents of the tube, after the combustion is finished, are mostly quicklime with some carbonate, since they slake strongly and effervesce slightly in dilute acid.

The following are some of the results obtained by the two methods. Soda-lime here signifies the mixture of about equal bulks of sodium carbonate and slaked lime. The combustions have been executed by Mr. E. H. Farrington.

	Theory.	Soda-lime.	Slaked lime.
Crystallised potassium ferrocyanide,	19.93	19.82	19.86
Anhydrous " "	22.80	22.78	22.83
Potassium ferricyanide, . . .	25.49	{ 25.42 25.46	{ 25.40 25.42
Strychnine,	8.38	...	{ 8.30 8.32
Hippuric acid,	7.81	7.79	7.83
Dried oak leaves,	1.81	1.76
Dried chestnut leaves,	1.54	1.63
Wheat middlings,	2.28	2.30
Dried peat,	2.03	1.94
Castor pomace,	4.54	4.53
"Fish and Potash,"	2.48	2.39
" " " another sample,	3.75	3.75
Superphosphate,	3.46	3.37
Bone,	3.93	4.02
" another sample,	6.70	6.61
Fish scrap,	7.16	7.12
" " another sample,	7.61	7.70
Dried blood,	{ 11.79 11.79	{ 11.88 11.79
" " another sample,	{ 11.18 11.23	{ 11.26 11.33

In the case of bone, fish, and superphosphates, a still closer agreement would probably have been obtained by the two reagents if the materials analysed had admitted of finer pulverisation and more accurate sampling.

A considerably larger number of comparisons have been made, but in no case, except that of strychnine, was the difference greater than is indicated by the determinations above given.

The combustion of strychnine is more difficult than that of the other substances named above, and for good results it is needful to use it in small quantities, as seen from the subjoined statement.

				Soda-lime.	Slaked lime.
Strychnine	. 0.5 gram:	tube 12-14 in.		{ 7.82 7.85	7.89 7.98
"	. 0.3 "	{ " 14 "		7.44	...
"	. 0.2 "	{ " 20-22 "		{ 8.14 8.05	8.14 8.20
"	. 0.2 "	" 20 "		8.14 ¹	8.25
"	. 0.1 "	" 20 "		...	{ 8.30 8.32

REVIEWS AND REPORTS.

THE EXTRACTION OF SULPHUR.²

Sulphur is found either in superficial deposits, the result of volcanic emanations, constituting the *sofataras*, or else at a considerable depth underground, associated with calcareous and bituminous marls, gypsum, celestite, etc., forming the sulphur mines, which are the most important sources of this material.

The principal mines are in Sicily and in continental Italy.

The ore is gotten out with picks and is transported from the mine on the backs of men. Its extraction is effected by the partial combustion of the sulphur. This causes heat enough to fuse the remaining portion, which then flows into a hollow in the ground from which it is collected. In Sicily the sulphur is treated in a kiln, termed the *calcaroni*. It consists of a wall enclosing an inclined circular area, on which the ore is placed. The heap is covered with a layer of spent material thick enough to keep the combustion from proceeding too rapidly, and spaces are left here and there for the insertion of fagots of wood. The *calcarone* ready, the fagots are lighted, and the access of air so regulated as to avoid active combustion and too high a temperature. After the operation has been in progress a certain length of time, the operatives begin

¹ Will and Varrentrapp's Soda-lime, made by Merck.

² Translated from a paper by M. Camille Vincent in the Bulletin de la Société chimique.

collecting the sulphur and continue it until the ore is exhausted. In this operation considerable quantities of sulphur dioxide are produced, and in consequence of the difficulty of regulating the draught, much sulphur is wasted. Great damage is caused to the surrounding country, and any cultivation of the ground within a certain radius of the burning places is prevented. So great is this nuisance that the government of Italy forbids "burning the ore" between the first of July and the thirty-first of December.

The *calcaroni* yield but 50 per cent. (at most 60 per cent.) of the sulphur contained in the ore, the rest serving as the fuel, and thus producing torrents of sulphur dioxide. The imperfections of this process have for a long time given rise to numerous attempts to devise a more rational and less costly method of extracting the sulphur by the employment of some other kind of fuel. Heated air, steam under pressure, superheated steam, and carbon bisulphide to dissolve the sulphur, have in turn been proposed for the purpose of obtaining the greater part of the sulphur without the production of sulphurous acid fumes.

In the first of these methods, a chamber of masonry is filled with the ore, and a current of warm gas, from a hearth fed with wood or coal, is sent into it. This prevents in great measure the production of sulphurous acid, but the action is slow and the mass of ore is irregularly heated. A large amount of fuel is used and the number of hands is increased, so that the economy over the old method is very small.

The use of steam seemed at first sight to offer the best solution of the problem, for its action is very simple and rapid, and the sulphur obtained of good quality. The yield is better than in the *calcarone* process, and no sulphur dioxide is produced.

But the advantages of this method are counterbalanced in great part by the extra expense of purchasing and maintaining the equipment, as well as furnishing the fuel. The apparatus necessary are the boilers for heating the water, tanks to receive the ore, and other accessories. The water available for supplying the boilers is bad, rapidly forming crusts, which increase materially the cost of maintenance. Besides, the proportion of fuel used is considerable, in consequence of the large amount of steam necessary to heat the ore, as well as the loss of heat due to radiation from the uncovered surfaces of boilers, tanks, etc. This process cannot be applied in all cases, for the increased yield will not compensate for the greater cost of operating.

The treatment by carbon bisulphide, though very rational *a priori*, presents inconveniences that make its use impracticable. This solvent volatilises very rapidly, making it difficult and dangerous to work with, besides causing a considerable loss of material.

These difficulties have prevented the various processes from being used to any great extent, so that the old method of the *calcarone* is the one still generally employed.

In 1805 Thomas proposed immersing the ore in salt solutions heated to a suitable temperature. Balard, in 1867, thought the water from the salt marshes, which is rich in magnesium chloride, might answer. And finally, in 1868, Dépérais took out a patent in Italy for the extraction of sulphur by the immersion of its ores in a liquid heated 10° or 20° above its fusing point. By this means it is separated from the earthy materials associated with it. He used a solution of calcium chloride. The apparatus consisted of a spherical boiler of 2000 litres capacity, furnished with a stop-cock for drawing off the liquid sulphur, and surmounted by a vertical cylindrical part, into which, with the aid of a pulley, a basket of perforated iron, filled with the ore, can be let down upon a grate.

The apparatus is placed in a furnace and heated directly, while the cylindrical portion is surrounded by the warm gases passing up the chimney. The basket of ore is let down into the solution of chloride of calcium heated to 130° . The sulphur melts, collects in the bottom of the boiler, and is drawn off by the stop-cock and poured into moulds. When the ore is exhausted the basket is raised and immediately immersed in water contained in another boiler heated in the same furnace. This was used to supply the place of that lost by evaporation in the first.

At that time chloride of calcium was comparatively dear, so that the patent could not be worked successfully, and was soon abandoned.

Very recently this process has been taken up by MM. de la Tour and Dubreuil and put into practice by them with success.

Chloride of calcium is now very cheap, in consequence of the rapid development of the soda industry (the ammonia process). It can be put down at the sulphur mines in Sicily at 9 francs per 100 kilos.

The apparatus of MM. de la Tour and Dubreuil consists of two rectangular tanks, holding about 2 cubic metres each ($2\text{ m.} \times 1.30\text{ m.} \times .75\text{ m.}$). The bottom of the tanks is inclined $\frac{1}{16}$. They are placed in the same furnace and heated alternately by the same fire, which is fed with coke, lignite or coal. The ore is placed in one of these tanks, in which is also placed a solution of calcium chloride boiling at 120° . Heat is then applied, the sulphur melts gradually, and is drawn off directly into moulds by means of a spigot.

The whole operation lasts about two hours. The end is reached when the sulphur ceases to flow. The calcium chloride solution is then drawn off into the other tank previously charged with ore. Half of the liquid flows through a communicating tube, the rest is received in a vat built in the ground and is raised by a pump. The gangue is washed to regain the salt which it has absorbed, and this dilute solution is used in filling the tanks as occasion demands. The heat is then directed upon the second tank, and the first is cleared and recharged. There is no interruption in the

work, and the heat from the fire is all utilised. The sulphur obtained contains only .1 per cent. or .2 per cent. of impurity, whereas that obtained from the *calcaroni* contains from 2 per cent. to 3 per cent. There is left in the gangue but 4 per cent. or 5 per cent. of the sulphur originally contained in the fresh ore.

In this treatment certain ores are completely disintegrated, in consequence of the fusion of the sulphur, which is then mixed with earthy matter. MM. de la Tour and Dubreuil in order to overcome this great inconvenience were compelled to change completely the plan of their apparatus. The new plan which they adopted is applicable to the treatment of ores of all kinds.

The tanks are built horizontal, and are divided longitudinally through the centre by a gutter with inclined sides, which collects the sulphur, and from which it is drawn. On its two sides iron gratings are built vertically to keep the ore from falling into it. These gratings are made of bars of sheet iron 2 mm. thick and 25 mm. wide, placed 3 mm. apart. By this new arrangement they can treat ores of all kinds, even the fine powder formed in mining the ore. This powder is very rich, and is known in Sicily as *sterri*. It was formerly left at the mines. This *sterri* is always richer than the average of the mined ore, for in getting the ore out, the rock breaks and divides along the lines of least resistance, which in this case are the veins of sulphur. On account of its friability the sulphur is reduced partially to dust and forms a large part of the mixture.

At the Tronica mine, in the province of Caltanissetta, in Sicily, the ordinary ore gives 21 per cent. of sulphur when treated by the calcium chloride method, while the *sterro* yields 72 per cent. The average yield of the Sicily ore, treated in the *calcarone*, is from 12 per cent. to 13 per cent. In some few cases it reaches 17 per cent.

On comparative treatment the same ores yielded from 10 per cent. to 12 per cent. by the *calcarone* process, and from 19 per cent. to 23 per cent. by fusion in chloride of calcium bath.

It has been known for a long time that ores very rich in sulphur acted badly in the *calcarone*. The combustion is too rapid, and the sulphur, browned and viscous from overheating, is hard to draw off. In order to treat such ores it is necessary to mix them first with inert material when the yield is not in accordance with the primitive richness of the ore. These rich ores are, on the contrary, treated advantageously in the chloride of calcium bath.

After the treatment of a large amount of *sterri*, MM. de la Tour and Dubreuil estimated the cost of extraction of a ton of sulphur at 12 fr. 75c. in the case of a mean yield of 33 per cent. of the weight of the ore.

The cost of treatment of one charge (about 1000 kilos) in their apparatus, is as follows:

35 kilos. fuel (coal mixed with lignite) @ 30 fr. per ton,	1 fr. 5c.
14 " chloride of calcium, 2 per cent. carried away by gangue after washing, @ 9 fr. for 100 kilos.,	1 25
Labor,	1 25
Unforeseen, general expenses, 20 per cent.,	70
Total,	4 fr. 25c.

Thus, in order to obtain a ton of sulphur, three charges must be worked, making the cost of extraction 12 fr. 75c. per ton.

An operation with *sterri* requires an hour and a quarter for fusion, a quarter of an hour for drawing the sulphur, and an hour and a half for washing the gangue and letting it drain, clearing the tank and putting the movable gratings back in place.

MM. de la Tour and Dubreuil have already introduced a number of their tanks in the sulphur region, principally for working up the *sterri*. There are three at the Tronica mine, in the province of Caltanisetta; two at the Grottarossa mine, in the same province; two at Pernice, near Recalmuto, and two at the mine Crocca.

The method just considered presents great advantages over the older methods:

1st. It allows the extraction of the greater part of the sulphur from ores of every kind, at a minimum cost for fuel.

2d. The extraction is effected regularly, protected from atmospheric influences.

3d. Work is carried on throughout the year, as no sulphurous acid fumes are formed.

4th. It permits the treatment of the ores according to the demands of the trade.

W. S. B.

STARCH AND ITS TRANSFORMATIONS UNDER THE INFLUENCE OF ACIDS.

The views concerning the transformation of starch into sugar by boiling with sulphuric acid, or the action of diastase, have been so contradictory that the nature of the changes which starch undergoes in this transformation has remained entirely open to question. Quite recently, however, F. SALOMON¹ has succeeded by a very elaborate investigation in placing the reaction on a satisfactory basis.

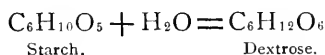
Musculus was of the opinion that by the action of diastase, as well as sulphuric acid, starch is split up into two molecules of dextrin and one molecule of sugar; and later the acid acts on the dextrin thus formed, though very slowly. The first decided contradiction to this view was furnished by Payen, who asserted that starch did not split up in the manner described by Musculus, either under the influence of diastase or sulphuric acid, but rather that there was a gradual transformation. The fact that these two opposed

¹ Journal für praktische Chemie, 28, 65.

views have been advocated by various subsequent investigators serves to show that considerable difficulty is involved in the settlement of the question. The announcement by Soxhlet of the inexactness of Fehling's sugar test showed that the key to this difficulty must be sought in improved methods for the determination of the substances which appear in the process. Salomon has, therefore, first studied the beginning and end products of the reaction, *i. e.* starch and dextrose, and also the intermediate products, "soluble starch," dextrin and maltose, particularly with regard to the analytical processes involved in their determination.

Starch.

The methods given in the text-books for the quantitative estimation of starch are based usually upon the conversion of starch into dextrose (glucose, starch sugar) with the aid of dilute sulphuric acid, and the subsequent determination of the sugar by reducing solution of copper. But Allihn has shown that starch is never entirely converted into sugar by this means, and that 95 per cent. is the maximum that can be converted into sugar by sulphuric acid under the most favorable circumstances. But if hydrochloric acid is used according to the method of Sachsse, a complete conversion may be effected. This method of Sachsse yields satisfactory results as regards the conversion of starch into sugar, but Salomon differs from Sachsse in the formula obtained by it for starch, *i. e.* $C_{36}H_{62}O_{31}$, containing one molecule of water more than required for a hexapolymer of $C_6H_{10}O_5$. Salomon has found by the specific gravity and specific rotatory power of the converted starch, and also by gravimetric determinations of the sugar by Allihn's method, that from 100 parts starch 111.1 parts of dextrose are obtained, a result which agrees very closely with the theoretical, supposing the reaction to be



The deviation from the proportion observed by Sachsse was probably due to insufficient drying of the specimens of starch used in the analyses.

The determination of the amount of moisture in starch is by no means as simple as might appear from casual observation. The author has found that if starch is dried at any given temperature between 100° and 130°, the loss of moisture is nearly constant for this temperature for the same variety of starch. As soon as the temperature rises above 120°, even at 125°, all the kinds of starch begin to turn yellow, and therefore a deeper decomposition undoubtedly begins at this point. But the loss of water is most constant at 120°. From the fact that starch dried at this temperature yields more sugar than that dried either below or above, the complete drying can be effected only at this temperature. It must be

allowed to cool in a sulphuric acid desiccator, as it will take moisture from calcium chloride. After the conversion of starch into sugar by the aid of hydrochloric acid, the sugar is determined by the gravimetric method of Allihn with the precautions observed by Soxhlet. If pure sugar solutions are used the results are identical with those given by Allihn, but if, on the contrary, the solutions contain other substances, good results can only be obtained when care is taken that nearly all the copper solution used is reduced. Good results may be obtained even in dilute solutions when the sugar is made from potato or rice starch, but with corn starch certain irregularities in the reduction can only be explained by supposing the presence of a reducing substance in corn starch or formed during its conversion into sugar. The numbers obtained with dilute solutions were too high, and only approached the theoretical amount when one per cent. solutions were used, so that an "after reduction," as it is called by Allihn, could not take place.

Dextrose.

The author makes use of the following facts in studying the transformation of starch into this substance:

1. Dextrose dissolves easily in water and dilute alcohol.
2. An aqueous solution of iodine effects no perceptible change in the sugar solutions.
3. The specific gravity of a solution containing 10 grams of dried dextrose in 100 cc. water is 1.0381.
4. The reducing power of dextrose may be conveniently estimated by Allihn's method.
5. The specific rotatory power of dextrose is: $\alpha_D^{20} = 58.68^\circ$.

A similar study of maltose shows: 1. Solubility in water and strong alcohol. 2. Indifference towards iodine. 3. 10 grams of dry maltose in 100 cc. water at 17.5° give a specific gravity 1.0390. 4. 1 gram dry maltose in 100 cc. water rotates the plane of polarisation 8° in a 200 mm. tube of the Jellet-Cornu apparatus. 5. 1 gram dry maltose corresponds to 1.13 grams of copper.

Soluble Starch.

This substance was first obtained by Jaquelin in 1840 by heating starch paste to 150° . Its importance in the present investigation lies in the fact that it is also formed by the action of dilute sulphuric acid on starch. It is a white, soft, bulky powder, insoluble in cold water, but easily soluble at 80–100 degrees, forming a clear, transparent liquid that has none of the pasty character of solutions of ordinary starch. The pure substance gives a deep blue color with iodine, but if care is not taken to separate dextrin the color is a red-violet. It does not affect Fehling's solution under the ordinary conditions of Allihn's method of sugar estimation. An aqueous 1 per cent. solution has a specific gravity of 1.0041. It rotates the plane of polarisation $+11.91^\circ$ in a 200 mm. tube of the Jellet-Cornu apparatus.

Dextrin.

The literature concerning dextrin contains many statements greatly at variance in regard to the properties of this substance. These inconsistencies seem to be due to the great difficulty of obtaining pure dextrin free from sugar or maltose, and also to the difference in the reaction with iodine which these impure specimens display. Pure dextrin may be obtained by the action of sulphuric acid on starch if care is taken to stop the process early enough. The solution thus obtained gives no reaction with Fehling's solution under the conditions of Allihn's method. By continued purification dextrin can be obtained which gives only a very slight brown-red color with aqueous iodine solution, and this color is so out of proportion to the amount of dextrin used as to satisfy the author that it is due to a slight admixture of sugar and that pure dextrin gives no color with iodine. Dextrin is precipitated from its aqueous solutions on the addition of alcohol. Its specific gravity in 10 per cent. solution is 1.038. The specific rotation in neutral aqueous solution is $[\alpha]_D^{20} = 216.5^\circ$, or 1 gram dissolved in 100 cc. water gives 11.3° in a Jellet-Cornu apparatus. This specific rotation appears to be greater in acid than in neutral solutions.

Examination of the Process of Starch Transformation.

With analytical data, the action of dilute sulphuric acid was studied in the following way: An apparatus was arranged in which a certain amount of starch solution could be boiled at a fixed concentration, and from which portions could be easily taken for analysis at regular intervals. These portions were examined as to their action on iodine solution, their rotatory power and specific gravity. As many as sixteen observations were recorded in one of these boiling processes which were sometimes continued for twenty-eight hours. By a study of the iodine reaction, and observing how the time of boiling and the concentration of the acid affect the reaction of iodine solution on the transformation products of starch, it is seen: 1. That the change from one color to another is very gradual. 2. That it always takes place in exactly the same order, *i. e.* from deep blue to violet, red-violet, red, red-brown, brown-yellow, yellow, and finally colorless. 3. That neither the complete extinction of the color nor the individual shades correspond exactly with the amount of sugar formed as shown by the rotatory power. The color changes may be ascribed to the soluble starch alone, and the color which this substance gives with iodine depends upon the concentration, the temperature, the amount of dextrin, and the degree of subdivision of the latter substance.

From considerations of the changes in rotatory power and the action of Fehling's solution it is seen that the conversion of starch proceeds more rapidly in proportion as the acid is stronger; by doubling the amount of acid the conversion is nearly twice as

rapid. The conversion is very gradual, proportional to the time, and becomes somewhat slower as the end of the process is approached. It proceeds in inverse proportion to the observed rotation, which changes nearly inversely as the reducing power until all the dextrin is converted into sugar, and longer boiling still decreases the rotatory power slightly. The end point is reached at 34.0° of the Soleil-Ventzke-Scheibler apparatus.

Another series of experiments shows that after boiling starch with sulphuric acid $2\frac{3}{4}$ hours, the solution contains soluble starch, dextrin, dextrose, and perhaps maltose.

By boiling for another hour the soluble starch disappears, and the examination of the specific gravity, reducing action and optical conduct, show that maltose is probably absent, and give data for calculating the proportion of dextrose and sugar. After the second boiling the quantities of sugar and dextrin are about equal. At the end of the fourth hour there is about twice as much sugar as dextrin, and then the proportion changes at a slower rate, until at the end of the seventh hour there is about seven times as much sugar as dextrin, but further than this the examination could not be carried with satisfactory quantitative results.

By studying the action of other acids on starch the author finds that organic acids are also able to effect the transformation into sugar. Oxalic acid particularly when used in equal amount with the sugar converts it entirely into sugar in three hours; a fact which is used largely in the actual manufacture of starch sugar.

Citric and tartaric acids require a much longer time than sulphuric acid for the transformation of starch even when used in much larger quantities, but they furnish chemically pure dextrose.

According to the experience gained in the course of the work, the action of sulphuric acid consists in transforming the starch molecule, which probably consists of a union of several groups $C_6H_{10}O_5$, into the simpler soluble starch, and this into dextrin. This phase of the process is accomplished with remarkable rapidity, so that the second phase, the hydration of the dextrin into sugar, begins almost at the same time.

Since the formation of sugar is intimately connected both with the time and also with the concentration of the acid, so that a double amount of acid converts twice as much starch into sugar in a unit of time, the process may be represented as very similar to the formation of ether.

Sulphuric acid unites with a certain amount of the dextrin, hydrates it, and gives it up again to unite with a new quantity of dextrin and convert it in turn into sugar.

D. T. D.

NOTES.

Historical Note concerning the Presence of Carbon in Phosphorus.

In connection with the observations of Mr. Keiser and myself which prove the presence of carbon in ordinary phosphorus, it is interesting to note the fact that this subject was actively discussed in the early part of the present century. The discussion was started by Proust¹ in 1799, who described a compound which he called phosphide of carbon (phosphure de charbon), obtained as a residue in purifying phosphorus. According to Proust, when the phosphide is treated with nitric acid a mixture of carbonic acid and the oxides of nitrogen is given off.

Later Steinacher² confirmed the observation of Proust, and stated that it was impossible to completely remove the carbon from phosphorus. The evidence which he put forward is, however, not convincing.

In 1812 Thenard³ stated in the most positive way that the purest phosphorus that could be made contained carbon; and that when phosphorus is burnt slowly in the air, not only phosphorous acid, but also carbonic acid is formed; though he adds that when phosphorus is burnt rapidly no carbonic acid is obtained.

In 1813 Vogel⁴ denied the presence of carbon in phosphorus, his opinion being based mainly on the fact that, according to him, no carbonic acid is formed when phosphorus is treated with nitric acid.

In 1816 Thomson⁵ described phosphide of carbon obtained from phosphorus, and even gave the results of an analysis which showed that the compound contained 38 per cent. carbon and 62 per cent. phosphorus.

Finally, in 1818, Davy⁶ stated that by treating phosphorus with chlorine he had convinced himself that it contained no carbon. Since that time the matter appears to have been dropped. Evidently this statement coming from Davy, who at that time was at the height of his renown, carried conviction with it.

It is difficult to see how the absence of carbon could be positively proved by Davy's method. Apparently Davy held that the chlorine would unite with the phosphorus and leave the carbon as such behind. But, if the carbon were in combination with the phosphorus, it might, and probably would, unite with chlorine,

¹ Scherer's *Journal der Chemie*, **7**, 234 (1801).

² Gehlen's *Journal der Chemie*, **1**, 679 (1803).

³ *Annales de Chimie*, 1812, 109; abstract in Schweigger's *Journal für Chemie und Physik*, **4**, 212.

⁴ Schweigger's *Journal für Chemie u. Physik*, **18**, 368.

⁵ *Philosophical Transactions*, 1818, Part 2.

⁶ *Ibid.* **7**, 109.

forming a compound which when mixed with the chlorides of phosphorus it would be difficult to detect.

It appears then that the only experiment in which all possible sources of error have been avoided is that of Mr. Keiser and myself, and though this experiment opens anew an old question, it at the same time furnishes a final answer.

I. R.

On the alleged Transformation of Brucine into Strychnine.

Sonnenschein¹ announced in 1875 that when brucine is gently heated with dilute nitric acid, carbonic acid gas escapes, while the solution contains a yellowish resin and strychnine, which may be extracted by saturating with potash and treating with ether. On the other hand, according to Laurent and Gerhardt and to Hofmann, there is formed in this reaction methyl nitrate and a nitrogenous base, cacotheline. The identity of the resin obtained by Sonnenschein with this latter is evident, and M. Hanriot has endeavored to verify the existence of strychnine among the products of the reaction. In operating, however, in precisely the same manner described by Sonnenschein, but with purified brucine, he has not been able to discover the slightest trace of strychnine, the qualitative reaction of which is, as is well known, extremely delicate. He therefore concludes that the strychnine found by Sonnenschein pre-existed in his incompletely purified brucine.

M. HANRIOT has further discovered that when brucine contains even as large a quantity as half its weight of strychnine the latter cannot be discovered by its ordinary reaction, so that it does not suffice to try a specimen of brucine by the reaction with sulphuric acid and potassium bichromate to conclude that it is free from strychnine.

If a mixture of brucine (2 parts) and of strychnine (1 part) be heated in the manner described by Sonnenschein, the strychnine can readily be discovered by its reaction after the brucine has been destroyed by the nitric acid; or more simply, if a mixture of the two bases in sulphuric acid, containing a drop of nitric acid, be allowed to stand in a watch-glass, strychnine can be discovered after two hours. A large number of substances are thus capable of masking the reaction of strychnine, among them morphine, quinine, and methyl alcohol, though this has a more feeble action.

It will be seen that the recognition of strychnine in brucine presents a certain amount of difficulty, and inasmuch as physiological properties have been attributed to brucine which resemble those of diluted strychnine, it becomes of interest to inquire whether the specimens of brucine operated with up to this time have really been free from strychnine. M. Hanriot is at present investigating the purification of brucine.—(*Comptes Rendus*, 97, 267.)

R. D. C.

¹ *Berichte der deutschen chemischen Gesellschaft*, 8, 212.

A Simple Method of Extracting Caesium and Rubidium Compounds from Hebron Lepidolite.

Lepidolite from Hebron, Maine, has been shown to contain caesium and rubidium in considerable quantities. The following is a simple and effective method of obtaining the compounds of these metals.

The mineral is pounded in an iron mortar until it feels soft to the touch; mixed in the mortar with an equal weight of fluor-spar, and the two ground together for a few minutes to secure intimate mixture. The mixture is transferred to a leaden dish, made into a thin paste with common strong sulphuric acid, and heated on a sand bath for two or three hours or until the mass is hard and dry.

When cold the mass is broken up, placed in a porcelain dish, and boiled out three times with water, the water in each case being poured, while hot, through a filter.

The filtrate contains caesium, rubidium and potassium as alums. These alums are about equally soluble in hot water, but at 17° the potash alum is nearly six times more soluble than the rubidium alum, and twenty-two times more soluble than the caesium compound (Redtenbacher). Hence it is easy, by means of these differences, to separate the rubidium and caesium compounds from the last traces of potassium, and from each other.

1000 grains of lepidolite, treated in the above manner, yield about 30 grains of caesium and rubidium alums.

The process seems to commend itself on account of: (1) Its cheapness—the only reagents used being common fluor-spar and sulphuric acid; (2) the short time required—but a single day; (3) avoiding the use of platinic chloride, and fusion of the mineral.

F. C. ROBINSON and C. C. HUTCHINS.

BOWDOIN COLLEGE, July 2, 1883.

The Production of Metallic Titanium by the Action of Sodium at Low Temperatures.

An experiment was made with a view towards forming titanium trichloride, Ti_2Cl_6 , by the action of sodium upon the tetrachloride, $TiCl_4$.

A small ignition tube was one-third filled with the anhydrous tetrachloride, and sodium in small pieces dropped in, in quantity sufficient to fill the tube nearly to the level of the liquid. The tube, after being sealed, was exposed to the action of a steam bath for 10 hours. At the end of this time the pieces of sodium were found to have a black coating of metallic titanium.

When heated to 130° the action became more rapid, the pieces of sodium still retaining their shape, but becoming somewhat honey-combed. At 150° a violent reaction took place, breaking the tube. The lumps remained of the same general form and dimensions as the lump of sodium used, but, after the experiment, they contained only a small central bit of sodium, the remainder being a thick crust of titanium.

Further experiments will be made with a view towards ascertaining the lowest temperature at which the metal can be produced.

F. C. ROBINSON and C. C. HUTCHINS.

BOWDOIN COLLEGE, July 2, 1883.

Concerning the Thiophene and Pyrrol Groups.

VICTOR MEYER continues his studies of the substances related to thiophene recently found by him in ordinary coal-tar benzene. He again calls attention to the remarkable resemblance of the derivatives of thiophene to the corresponding ones of benzene. As monobrom-thiophene can be obtained only with difficulty he has been unable to make methyl-thiophene by Fittig's method. On the other hand, it is probable that in coal-tar xylene as well as toluene the homologues of thiophene are contained. That contained in toluene has been separated, though not in pure condition, and it has been shown to be methyl-thiophene, as was anticipated. To obtain this substance the sulphuric acid extracts of about two tons of toluene were worked up. By distilling the lead salt of the sulphonic acid with ammonium chloride, several kilograms of an oil were formed, which after a few distillations boiled at 110° . This was found to consist of about 15 per cent. of methyl-thiophene and 85 per cent. of toluene. Although it was found to be impossible to isolate the methyl-thiophene in pure condition, its dibrom-substitution product, $C_4HS \begin{Bmatrix} CH_3 \\ Br_2 \end{Bmatrix}$, was obtained without difficulty.

Thiophene is the mother-substance of a large number of beautiful coloring matters. In general, it was shown that ketones, which contain only carbon, oxygen and hydrogen, give colored products, if they contain the group $CO-CO$. Simple ketones or those double ketones which do not contain the two carbonyl groups in direct combination do not give colored products. Colored products have been obtained from: phenyl glyoxylic acid and thiophene (violet red); benzil and thiophene (blue); phenanthrene-quinone and thiophene (green); phenanthrene-quinone and methyl-thiophene (violet); alloxan and thiophene (deep blue).

Meyer has also shown that pyrrol, C_4H_5N , acts towards the ketones very much in the same way that thiophene does, especially in the matter of yielding colored products. This fact points to an analogy between the structures of the two substances. If thiophene be regarded as benzene in which two CH groups are replaced by a sulphur atom, as represented in the formula, $\begin{array}{c} CH=CH \\ | \\ CH=CH \end{array} > S$, pyrrol may be regarded as benzene in which two CH groups are replaced by NH as represented thus, $\begin{array}{c} CH=CH \\ | \\ CH=CH \end{array} > NH$. — (*Berichte der deutschen chemischen Gesellschaft*, 16, 2968.)

The Liebig Monument.

Last November the beautiful monument of Liebig which had been unveiled in Munich only a few months previously, was found to have been horribly disfigured by a large number of stains, about three hundred in number, which apparently had been applied by some human fiend standing upon the marble pedestal. The city government called in Professors von Pettenkoffer and Baeyer and Dr. C. Zimmermann, all of the University, to determine the nature of the stains and, if possible, to remove them. They soon found that the principal substance which had been used was nitrate of silver with which permanganate of potassium had been mixed. The stains had worked their way into the marble several millimeters.

The committee experimented in a number of ways upon pieces of marble stained with the substances believed to have been used, and succeeded in devising a method for completely removing the stains without injury of any kind to the marble. The method consists in first converting the metals, silver and manganese, into the sulphides and then dissolving these in a solution of potassium cyanide. In order to apply the reagents to the statue, they were mixed with finely powdered porcelain clay so as to form a paste. A paste saturated with ammonium sulphide was first applied to all the spots and allowed to remain for twenty-four hours. It was then removed and replaced by a fresh paste containing the same reagent, which also was allowed to remain for a day. After removing this paste the spots were washed with water, and a paste containing a concentrated solution of potassium cyanide applied. This was once removed and renewed, and the spots then found to have disappeared entirely. The statue is now again in perfect condition, subsequent exposure to the sunlight having produced no effect upon the cleansed parts.—(*Berichte der deutschen chemischen Gesellschaft*, **17**, 230.)

At the last annual meeting of the German Chemical Society, Professor Wolcott Gibbs, of Harvard University, was elected an honorary member of the society. Professor Gibbs is the first American upon whom this honor has been conferred. Its significance will be appreciated when it is stated that the list of honorary members is a very short one and includes such names as Bunsen, Kopp, Berthelot and Frankland.

A few friends of Professor A. W. Hofmann have had a gold medal prepared to be presented to him in commemoration of his visit to this country. Upon one side is a very good bas-relief profile of Hofmann, and upon the other the simple inscription: "To A. W. Hofmann: from his friends and admirers in the United States of America, October, 1883." Bronze copies of the medal have been prepared for the subscribers to the fund.

AMERICAN CHEMICAL JOURNAL.

Contributions from the Chemical Laboratory of Harvard College.

XXXVIII.—ON CERTAIN SUBSTANCES OBTAINED FROM TURMERIC.¹

BY C. LORING JACKSON AND A. E. MENKE.

Owing to the difficulty of preparing curcumin, and the very unmanageable nature of the products obtained from it and from turmerol, we have not made as much progress in the study of these substances as we had hoped. In fact, we should not publish our results at the present time, were it not that we cannot continue the work together at all, and neither of us will be able to return to it for at least a year; we have therefore decided to collect in the following papers all the results we have obtained up to this time, although many of them are very fragmentary, and others consist only in indications which may prove useful in future work.

IV. CURCUMIN.

Action of Acetic Anhydride on Curcumin.

Monacetcurcumin, $C_{14}H_{18}(C_2H_3O)O_4$.—This substance is formed by the action of acetic anhydride and fused sodic acetate on curcumin, probably also by the action of acetylchloride. As has been stated in a previous paper,² it forms an uninviting brown

¹ Communicated by the Authors from the Proceedings of the American Academy of Arts and Sciences.

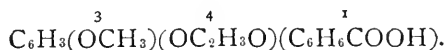
² This Journal, **4**, 90; and Proceed. Amer. Acad. **17**, 123.

resin, which we have not as yet succeeded in bringing into a crystalline condition; but nevertheless it can be obtained in a state of purity by the following method: Curcumin is heated on the water-bath with a slight excess of acetic anhydride and a little fused sodic acetate, for about sixteen hours, in a flask with a return-cooler; the dark brown viscous product is then dissolved in a little glacial acetic acid, and precipitated with water; after repeating the solution in acetic acid, and precipitation with water, the yellowish-brown precipitate is washed until free from acetic acid, and dried *in vacuo*.

0.1710 gram of substance gave 0.4178 gram of carbonic dioxide and 0.0922 gram of water.

	Calculated for $C_{16}H_{16}O_5$.	Found.
Carbon	66.67	66.62
Hydrogen	5.55	5.99

Properties.—A viscous brown mass without definite melting-point, although it shrinks together at 58° – 60° , but it does not become fully liquid below 100° . It is soluble in alcohol and glacial acetic acid, essentially insoluble in ligroine and carbonic disulphide, slightly soluble in ether and in benzene; but its solubility in the latter is greater than that of curcumin. It dissolves in strong sulphuric acid with a blood-red color like that produced by curcumin. Aqueous sodic hydrate dissolves it, forming a red solution, which becomes decomposed, with the formation of ill-defined black products, when allowed to stand exposed to the air; a mixture of alcohol and sodic carbonate was reddened instantly by the substance, showing that the acetyl group had replaced the hydrogen of the phenol hydroxyl, as was to be expected; that is, its formula would be



As has been stated already,¹ the substance gave unsatisfactory results when submitted to oxidation with potassic permanganate.

Diacetcurcumin, $C_{14}H_{12}(C_2H_3O)_2O_4$.—On one occasion the process described above yielded a yellow crystalline product instead of the brown viscous monacetcurcumin. The coming of the vacation interrupted our work before we had succeeded in determining the conditions on which the formation of this substance depends, the few experiments which we had time to try giving invariably monacetcurcumin; we must, therefore, for the present,

¹ *Loc. cit.*

confine ourselves to describing the properties and analysis of the substance. After the removal of the acetic anhydride and sodic acetate by treatment with water, it was purified by washing with alcohol and crystallisation from glacial acetic acid, dried at 100° , and analysed.

0.2230 gram of substance gave 0.5348 gram of carbonic dioxide and 0.1090 gram of water.

	Calculated for $C_{18}H_{18}O_6$.	Found.
Carbon	65.45	65.39
Hydrogen	5.45	5.43

Properties.—It crystallises from glacial acetic acid in rosettes of a vivid yellow color without the orange shade of curcumin, which are made up of very characteristic rhombic plates; melting-point 154° . It is more soluble in glacial acetic acid than in any other solvent, especially when the acid is hot; less soluble in alcohol than curcumin; slightly soluble in ether and benzene; essentially insoluble in ligroine and carbonic disulphide. Strong sulphuric acid dissolves it, becoming blood-red in transmitted light, green like rosaniline in reflected light; the red color is somewhat more purple than that produced by curcumin. Sodic hydrate in aqueous solution acts upon it very slowly, and not rapidly, even if dissolved in dilute alcohol; the red solution thus obtained gives with hydrochloric acid a viscous brown mass with a low melting-point, which seems to be impure monacetcurcumin. Sodic carbonic and alcohol give an orange solution looking like that of potassic dichromate. According to the formula given by us to curcumin in our first paper, this substance should be a mixed anhydride of curcumin and acetic acid, with the other acetyl group attached to the phenol oxygen, as in the monacet-compound,—a constitution which would be expressed by the following formula:



That the carboxyl group is affected by the introduction of the second acetyl is shown by the fact that alkaline reagents act upon it only after some time, and then evidently decompose it; whereas the monacet-compound is attacked by them instantly, and the action consists only in the formation of a salt: but, on the other hand, the substance is more stable than acid anhydrides are usually, as is shown by this very action with alkalies, and by the fact that it can be boiled with water for many hours without

undergoing any change in melting-point, or the formation of any soluble acid.

Action of Phosphoric Oxychloride on Curcumin.

Of all the reactions of curcumin, which we have observed, this is by far the most striking, and we have decided therefore to describe it at some length, although we have not succeeded in determining the nature of the substance formed. If a few drops of phosphoric oxychloride are added to some curcumin suspended in ligroine, its orange-yellow color is converted instantly into a rich reddish purple, which in reflected light appears bronze-green with a metallic lustre, between the colors of rosaniline and Hofmann's violet. To prepare the substance in quantity, the curcumin was rubbed in a mortar with phosphoric oxychloride diluted with ligroine and afterward washed repeatedly with ligroine; the dark purple viscous mass thus obtained was dried in a desiccator over sulphuric acid, lime, and paraffine. This treatment, the best which we could devise, was usually far from effectual, as in every case but one the substance contained phosphorus, and was invariably converted during drying into a black mass having very different properties from the purple viscous substance at first obtained. The analysis of the substance free from phosphorus gave results less than one per cent. higher than those required by curcumin, and this was confirmed by the analysis of one of the preparations containing phosphorus, after the phosphorus present had been calculated as phosphoric acid, and subtracted from the weight of the substance.

The properties of the purple product are quite as striking as its formation from curcumin; for the addition of water converts it again into curcumin, and the change from purple to orange-yellow is instantaneous. That curcumin was formed in this case was shown by the melting-point, 178° . Alcohol also changes the color instantly from purple to yellow; but the product is much more soluble in alcohol than curcumin, and is possibly its ethyl ether. Ether acts in the same way, leaving, on evaporation, a viscous red mass; in ligroine and benzene it is essentially insoluble. By standing even in a desiccator it is gradually decomposed—more rapidly at 100° —into a black mass, which is unaffected by water, but soluble in alcohol or sodic hydrate, forming dark solutions. Owing to the uninviting properties of this decomposition product it was not studied further.

It is highly probable that the blood-red color imparted to strong sulphuric acid by curcumin is due to this substance, as curcumin is deposited when this solution is diluted. As to the nature of the purple substance, our analyses show nothing; but its easy conversion into curcumin by the addition of water indicates that it is an anhydride, and we are inclined to believe that the carboxyl of the curcumin alone is involved in the reaction, because we obtained a similar but somewhat redder color when monaceturcumin was treated with phosphoric oxychloride.

In our first paper on curcumin we assigned to it the formula



Our work since then has been directed toward the determination of the structure of the side-chain $\text{C}_6\text{H}_6\text{COOH}$, and, although we have not succeeded in proving anything about it definitely, we may be allowed to state that our results can be explained by the assumptions that the carboxyl is attached to the carbon atom next but one to the benzene ring, and that in the remainder of the side-chain some of the carbon atoms are united to form a ring.

TURMEROL.

In our first paper on this subject we mentioned that, although turmerol is converted into terephthalic acid by treatment with an excess of a hot solution of potassic permanganate, the same reagent produces, when cold and not in excess, one or more apparently new acids. In the following paper we describe our study of the product of this reaction, a complex mixture of acids, from which we have succeeded in isolating two new acids,—one having the formula $\text{C}_{11}\text{H}_{14}\text{O}_2$, which we propose to call turmeric acid; the other either $\text{C}_{10}\text{H}_{12}\text{O}_4$ or $\text{C}_{10}\text{H}_{10}\text{O}_4$, to which we would give the name apoturmeric acid.

In order to obtain this product, a little turmerol was allowed to stand at ordinary temperatures with a moderately strong solution of potassic permanganate until the latter was reduced. The operation was carried on in large beakers, and the yield seemed to be better when not more than 500 cc. of permanganate solution were used in each oxidation, than when larger quantities were employed; with this amount the action came to an end in about three days. After the liquid had become colorless, the oxide of manganese and

unaltered oil were removed by filtration, and again treated with permanganate solution; this treatment being repeated until the permanganate ceased to act, when it was found that the oxide of manganese was essentially free from organic matter, and therefore that the entire product was contained in the aqueous filtrate. The mixed filtrates from a number of operations were then concentrated on the water-bath, acidified with sulphuric acid, extracted several times with ether, and the extract, a black tarry liquid, distilled with steam, when a yellow oil (A) passed over with some difficulty; this was mostly turmeric acid. The residue in the flask (B) contained a tarry substance and apoturmeric acid, which not infrequently separated in white crystals as the solution cooled.

Upon distilling with steam the solution left after extraction with ether, it yielded a strongly acid distillate containing a little of the yellow oily acid, from which it was freed in great part by extracting it five times with ether. It was then boiled with baric carbonate to convert it into a barium salt, which crystallised, after it had evaporated spontaneously nearly to dryness; the crystals, freed from mother-liquor by pressure between filter-paper, were nearly pure baric acetate, as shown by the following analysis:

1.1745 grams of the air-dried salt lost 0.0661 gram when dried at 100°.

	Calculated for $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$.	Found.
Water	6.59	5.63

1.1038 grams of the dried salt gave 0.9974 gram of baric sulphate.

	Calculated for $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$.	Found.
Barium	53.73	53.13

As, however, a solution of the silver salt blackened much more easily than argentic acetate should, and crystallised at first in balls made up of radiating needles, although after one or two recrystallisations attended by blackening it gave the flattened needles characteristic of argentic acetate, we suspected that there might be some other acid present, the barium salt of which had been removed in the mother-liquors, and resorted to fractional acidification with sulphuric acid to settle this point. For this purpose a quantity of the acid distillate, after treatment with ether, was converted into the calcium salt and treated with one-third of the amount of sulphuric acid necessary to set free all the acid it contained; it was then distilled with steam as long as the distillate

showed an acid reaction. The residue in the flask was treated twice successively with the same amounts of sulphuric acid, and the first and third fractional distillates converted into calcium salts.

I. 0.3582 gram of salt from the first fraction gave 0.2894 gram of calcic sulphate.

II. 0.2281 gram of salt from the third fraction gave 0.1980 gram of calcic sulphate.

	Calculated for $\text{Ca}(\text{C}_9\text{H}_5\text{O}_2)_2$.	I.	Found.	II.	Calculated for $\text{Ca}(\text{C}_9\text{H}_5\text{O}_2)_2$.
Calcium	25.32	23.76		25.54	21.50

From these numbers it appears that there is no large amount of any acid except acetic present, and the blackening and different crystalline forms of the silver salt were probably due to a trace of turmeric acid which could not be removed by ether.

As it was possible that a neutral lactone might have been formed, a portion of the acid liquid was boiled with baric carbonate, distilled with steam, and the neutral distillate boiled with baric hydrate for some time; as after removing the baric hydrate with carbonic dioxide there was no residue on evaporation, no lactone was formed.

The formation of carbonic dioxide was determined by a special experiment, in which a portion of turmerol was oxidised out of contact with the air; upon acidifying with sulphuric acid a gas was given off, which gave a copious white precipitate with lime-water.

A. Study of the Distillate obtained from the Ether Extract with Steam.

This consisted principally of water, with a few yellow or brown oil-drops floating in it. It was extracted with ether, and the extract, which had acid properties, boiled with water and calcic carbonate. The solution of a calcium salt thus obtained, when allowed to evaporate spontaneously, deposited spherical collections of white needles and a yellow viscous substance somewhat more soluble than the crystals.

The crystalline body proved to be the calcium salt of the new acid, which we have called turmeric acid, after it had been purified by repeated crystallisation from water, which is tedious in the highest degree, as all the solutions and evaporations have to be carried on at ordinary temperatures; in fact, it took us more than a

year and a half to prepare and purify the four or five grams of this substance which have served for the present research.

In regard to the nature of the viscous non-crystalline salt we cannot speak with certainty, as we were unable to obtain it free from calcic turmerate; but we are of the opinion that it is a salt of an isomeric acid, as an analysis of the salt, which had not been purified by crystallisation, gave 8.12 per cent. of calcium instead of 8.93 calculated for calcic turmerate, and the acid set free from the amorphous salt remained liquid even at -5° , while turmeric acid solidifies at ordinary temperatures.

The total yield of mixed calcium salts cannot be more than one or two per cent. of the turmerol oxidised, and the proportion of amorphous salt in this product is comparatively small.

Turmeric Acid, $C_{11}H_{14}O_2$.—The calcium salt prepared and purified as just described was treated with hydrochloric acid, and then extracted with ether. On evaporating off the ether, a yellowish oil was left, which crystallised on standing, and gave the following analytical results after being dried *in vacuo*:

I. 0.2198 gram of substance gave 0.5954 gram of carbonic dioxide and 0.1586 gram of water.

II. 0.1320 gram gave 0.3584 gram of carbonic dioxide and 0.0960 gram of water.

	Calculated for $C_{11}H_{14}O_2$.	I.	Found.
Carbon	74.16	73.87	74.04
Hydrogen	7.86	8.02	8.08

Properties.—The turmeric acid, as at first precipitated, is an oil, which gradually solidifies in long white branching needles, or crystalline masses, with a faint smell like cocoanut; freed from oil by pressing between the filter-paper it melts at 34° – 35° ; it is slightly soluble in water, very freely in all the other common solvents except methyl alcohol, in which, however, it is readily soluble, so that it was found impossible to crystallise it from this or any other solvent; it distils slowly with steam, and is a monobasic acid. When oxidised with a hot solution of potassic permanganate, not in too great excess, it gives the apoturmeric acid, which will be described later in this paper.

Calcic Turmerate, $Ca(C_{11}H_{13}O_2)_2 \cdot 3H_2O$.—The preparation and purification of this salt have been described in connection with the manufacture of turmeric acid. For analysis it was dried, at first *in*

vacuo, and afterward at 100° or 110° , when several agreeing analyses gave the percentage of calcium 10.78–11.13, whereas calcic turmerate contains only 10.15 per cent. of calcium. This led us to suspect that the salt had undergone a constant decomposition at this temperature, which we were the more inclined to do, because at first it lost weight very rapidly, but later the loss dropped to a few milligrams a day, and more than a week of continuous heating was necessary to obtain a constant weight, while at the same time the salt gradually became brown and viscous. We have therefore calculated our results upon the salt dried *in vacuo*, and these agree very well with the amount of calcium in calcic turmerate containing three molecules of water of crystallisation.

I. 0.3131 gram of substance dried *in vacuo* gave 0.0970 gram of calcic sulphate.

II. 0.2993 gram gave 0.0912 gram of calcic sulphate.

	Calculated for $\text{Ca}(\text{C}_{11}\text{H}_{13}\text{O}_2)_2 \cdot 3\text{H}_2\text{O}^{\circ}$	I.	Found.	II.
Calcium	8.93	9.11		8.96

Properties.—It forms spherical collections of white radiating needles looking like chestnut-burrs; the purer the salt the more distinct are the separate needles. When boiled with water it melts to a viscous mass, which is then acted on by the water only very slowly; it is therefore advisable to dissolve it in the cold.

7.861 grams of the solution saturated at 16° gave 0.0344 gram of calcic sulphate. Therefore a saturated solution at 16° contains 1.27 per cent. of $\text{Ca}(\text{C}_{11}\text{H}_{13}\text{O}_2)_2$.

The salt is also soluble in alcohol, and is decomposed by a heat of 100° – 110° , as already stated.

The behavior of a solution of the calcium salt with various reagents was also studied, and it was found to give a white flocculent precipitate with aluminic chloride; a similar reddish-brown precipitate with ferric chloride; heavy white precipitates with mercurous or plumbic salts, the plumbic salt melting under boiling water, and forming, when prepared in quantity, an uninviting yellowish viscous mass; cupric nitrate produced pale-blue flocks, and argentic nitrate a heavy white precipitate somewhat soluble in water; the other common reagents gave no characteristic precipitates.

An attempt was made to prepare and analyse the *silver salt*, but we did not succeed in purifying it, since its solubility in water is so great that the impurities could not be removed by washing without

using a larger amount of substance than was at our disposal; and it was impossible to recrystallise it from water, as its solutions decomposed with great ease. An imperfectly washed specimen gave a result which approaches that required by theory.

0.1932 gram of the salt dried *in vacuo* gave 0.0750 gram of silver.

	Calculated for $\text{AgC}_{11}\text{H}_{13}\text{O}_2$.	Found.
Silver	37.89	38.82

The *barium salt* resembled the calcium salt in that it formed little balls of radiating needles, but showed a much greater tendency to separate in a viscous state, so that it was hard to obtain it crystallised.

The behavior of the *zinc salt* is very characteristic; when a solution of it is prepared by boiling the acid with water and zinc oxide, allowing the liquid to cool, and filtering, the clear solution thus obtained becomes turbid, when warmed even to temperatures far below the boiling point, but clears up again as the liquid cools. The salt could be obtained only as a viscous mass.

B. Study of the Residue from Distillation with Steam.

The flask-residue, after the turmeric acid had been distilled off with steam, contained a black tarry substance, and not infrequently a white crystalline acid, which can be separated from the tar by treatment with boiling water. On extracting with ether the aqueous mother-liquor, from which the white acid had crystallised, a third substance, yellow and buttery, was obtained. All these substances are acids, but we have been unable to bring the black tarry acid or the yellow buttery one into a state fit for analysis, and can only say that the very ill-defined calcium salt of the former contained 1.69 per cent. of calcium, while the latter gave on oxidation an acid melting near 180° , which was not phthalic acid, and was formed in such small quantity that we were unable to determine whether it was a pure substance or only a mixture of apoturmeric acid with some impurity.

Apoturmeric Acid.—The white crystalline acid was separated from its impurities by crystallisation from boiling water, till it showed a constant melting-point. The same acid is obtained by oxidising calcic turmerate with a hot solution of potassic permanganate, and a good part of the substance used for analysis was prepared in this way; the yield, however, was so small, not over

10 per cent. of the turmeric acid used, that we have been unable to determine even its formula with certainty, as will be seen from the following analyses.

0.1138 gram of substance gave 0.2582 gram of carbonic dioxide and 0.0590 gram of water.

	Calculated for $C_{10}H_{10}O_4$.	Found.	Calculated for $C_{10}H_{12}O_4$.
Carbon	61.86	61.87	61.22
Hydrogen	5.15	5.76	6.12

The *calcium salt* made by boiling the acid with calcic carbonate and water gave the following results:

I. 0.2274 gram of salt dried *in vacuo* lost 0.0304 gram when heated to 100° .

II. 0.1390 gram lost 0.0186 gram when heated to 100° .

	Calculated for $CaC_{10}H_8O_{42}H_2O$.	I.	Found.	II.	Calculated for $CaC_{10}H_{10}O_{42}H_2O$.
Water	13.43	13.36		13.39	13.33

0.1826 gram gave 0.3370 gram of carbonic dioxide, 0.0758 gram of water, and 0.1016 gram of calcic sulphate.

	Calculated for $CaC_{10}H_8O_4$.	Found.	Calculated for $CaC_{10}H_{10}O_4$.
Carbon	51.72	50.32	51.29
Hydrogen	3.40	4.61	4.27
Calcium	17.24	16.36	17.10

The *barium salt* prepared like the calcium salt gave a result which is not in harmony with the preceding.

0.2704 gram of salt dried at 100° gave 0.1742 gram of baric sulphate.

	Calculated for $BaC_{10}H_8O_4$.	Found.	Calculated for $BaC_{10}H_{10}O_4$.
Barium	41.64	37.87	41.39

If, however, we suppose that the salt retained two molecules of water at 100° , the result agrees very well with the calculated per cents.

	Calculated for $BaC_{10}H_8O_{42}H_2O$.	Found.	Calculated for $BaC_{10}H_{10}O_{42}H_2O$.
Barium	37.53	37.87	37.32

But this supposition is, to say the least, improbable, as the calcium salt loses its water easily at 100° ; unfortunately, we did not have enough of the acid to repeat the analysis of the barium salt.

Properties.—The apoturmeric acid separates from its solution in boiling water as a white, rather stiff, woolly mass, which renders the whole solid, if the solution was a strong one; it melts at 221° , and is easily soluble in alcohol, ether, and boiling water; nearly insoluble in cold water.

Ammonic apoturmerate is not very freely soluble, and gives the following characteristic precipitates: With plumbic acetate, white flocculent; with cupric sulphate, whitish green,—both soluble in an excess of the precipitant; with mercurous nitrate, white flocks; with ferric chloride, yellowish white; with argentic nitrate, a heavy white precipitate, slightly soluble in boiling water. With the other common reagents it gives no precipitates at all, or very slight white ones.

Several attempts were made to oxidise the apoturmeric acid, but they gave no satisfactory result. The acid was attacked only with difficulty either by potassic permanganate or chromic anhydride, and the only insoluble substance left after the oxidation was simply undecomposed apoturmeric acid. In no case have we observed the formation of terephthalic acid from apoturmeric, or from carefully purified turmeric acid; but this acid has appeared when a calcic turmerate containing the non-crystalline impurity was oxidised. We should therefore ascribe the formation of terephthalic acid from turmerol by violent oxidation rather to this substance than to the turmeric acid formed; but our experiments must be repeated on a larger scale before we can consider this point finally settled.

It is to be regretted that we were unable to settle definitely the composition of the apoturmeric acid, as this would have thrown much light on the constitution of turmeric acid; as it is, it is not worth while to advance any hypotheses on this subject.

We may add one more observation in reference to turmerol, viz. isobutylturmerol does not give an addition-product with bromine, but there is formed with evolution of hydrobromic acid a most uninviting unstable viscous oil.

XXXIX.—ON THE ACTION OF PHOSPHORUS TRICHLORIDE ON ANILINE.

BY C. LORING JACKSON AND A. E. MENKE.

The only paper on this subject which we have been able to find was published by Tait in 1865;¹ in it he describes the product of the action of phosphorus trichloride on aniline as a white salve-like mass easily soluble in water, alcohol and ether, which, when freed from an excess of aniline, had the composition $(C_6H_5NH)_3P_3HCl$, gave a chlorplatinate and several double salts, but yielded no satisfactory result when he attempted to set free the base.

We were induced to take up the study of this reaction by the hope that a further investigation of Tait's substance might lead to interesting results; but in this we were disappointed, as we have not succeeded in obtaining it, and, as far as our experiments go, are inclined to think it must have been a mixture instead of a definite compound. At the same time, we cannot state with absolute certainty that it is not present in the product formed when a decided excess of aniline is used, since the impossibility of continuing our work after the beginning of the summer vacation prevented us from making the investigation of this product as thorough as we wished. For the same reason other parts of this research can be published only in a very fragmentary and imperfect condition.

The isolation of the compounds containing phosphorus formed by the action of phosphorus trichloride on aniline, in the proportion of one molecule to three, is surrounded by difficulties which we have found insurmountable; but, in spite of this, our experiments have determined with a fair degree of certainty the nature of these compounds, as will appear from the following general statement of our results, and the argument which can be based upon them.

When aniline is added to phosphorus trichloride in the proportion of three molecules of the former to one of the latter, the product, a variable mixture of aniline chloride and a substance containing phosphorus, gives a clear solution with water or alcohol.

¹ Jahresbericht der Chem. 1865, 411. Instit. 1865, 254.

If, however, this product is heated, a waxy mass is obtained, which is soluble in alcohol; but water throws down from this solution a white precipitate having the formula $(\text{C}_6\text{H}_5\text{NH})_2\text{PHO}$. Of the three most probable products of the reaction of phosphorus trichloride and aniline,

- (1) $\text{C}_6\text{H}_5\text{NHPCl}_2$,
- (2) $(\text{C}_6\text{H}_5\text{NH})_2\text{PCl}$,
- (3) $(\text{C}_6\text{H}_5\text{NH})_3\text{P}$,

only (2) could yield $(\text{C}_6\text{H}_5\text{NH})_2\text{PHO}$ by the action of water or alcohol, and we therefore infer that $(\text{C}_6\text{H}_5\text{NH})_2\text{PCl}$ exists in the product after it has been heated. On the other hand, this substance cannot exist in the original product, as this dissolves in water without residue, whereas $(\text{C}_6\text{H}_5\text{NH})_2\text{PCl}$ is converted by water into the insoluble $(\text{C}_6\text{H}_5\text{NH})_2\text{PHO}$; but it must be formed from one of the constituents of the crude substance during the heating. Of the two probable products of the reaction, (1) and (3), mentioned above, it is hard to see how (3), $(\text{C}_6\text{H}_5\text{NH})_3\text{P}$, by heating with aniline chloride, could be converted into $(\text{C}_6\text{H}_5\text{NH})_2\text{PCl}$, while (1), $\text{C}_6\text{H}_5\text{NHPCl}_2$, could easily undergo this change under these conditions; from which we conclude that $\text{C}_6\text{H}_5\text{NHPCl}_2$ and aniline chloride are the products of the action of aniline on phosphorus trichloride under the conditions mentioned. This conclusion is supported by the fact that alcohol or water acts violently on the original product forming aniline phosphite, and it is highly improbable that $(\text{C}_6\text{H}_5\text{NH})_3\text{P}$ would give such a violent reaction.

The remainder of this paper contains a detailed account of the experiments on which the above conclusions are based, a description of the properties and behavior of the new substance $(\text{C}_6\text{H}_5\text{NH})_2\text{PHO}$, and a somewhat fragmentary account of two crystalline substances formed by boiling the crude product with an excess of aniline, one of which may be a derivative of $(\text{C}_6\text{H}_5\text{NH})_3\text{P}$, although this point needs confirmation by further experiments.

Action of Phosphorus Trichloride on Aniline.

When aniline is added to phosphorus trichloride, the reaction is attended with so much heat, that each drop of the aniline hisses like red-hot iron in water when it touches the trichloride; and, if the substances are mixed in about the proportion of three mole-

cules of aniline to one of the trichloride, the product is a hard white solid, with no trace of the salve-like consistency described by Tait. It was proved to be a mixture by the following analyses of three different preparations, which were freed from an excess of either reagent by washing with ether before analysis.

	I.	II.	III.
Carbon	50.82	54.41	43.59
Hydrogen	6.28	7.07	7.10
Chlorine	19.38	23.15	...
Phosphorus	5.48	2.92	...

In the hope of isolating the phosphorus compound, the action of various solvents on the mass was studied,—of all the common solvents, water, alcohol, methyl alcohol, and acetone were the only ones in which it was not essentially insoluble; but, as we found that acetone dissolves aniline chloride, there was no prospect of achieving the purification of the phosphorus compound by its means, and either water or alcohol decomposed it, giving a clear solution,¹ which, on evaporation, left a viscous residue, apparently composed of chloride and phosphite of aniline, as it deposited crystals of the former after standing for some time, and upon solution in water and addition of plumbic acetate gave a heavy white precipitate, which, freed from plumbic chloride by washing with hot water, was proved to be plumbic phosphite, by the following analysis:

0.6986 gram of the salt gave 0.7380 gram of plumbic sulphate.

	Calculated for PbHPO_3 .	Found.
Lead	72.13	72.16

From this result it is probable that no anilidophosphorus acid was formed.

From what has been said it appears that the product described above differs from Tait's in consistency, in its solubility in ether, and in composition; but if, instead of fulfilling the conditions given above, the trichloride is added to a large excess of aniline, a substance is obtained which resembles Tait's in its salve-like consistency and the fact that it gives a considerable extract with ether; at the same time we cannot think that it has the composition ascribed to it by him, because our analyses given above show that

¹ When water was used there was sometimes a slight residue of $(\text{C}_6\text{H}_5\text{NH})_2\text{PHO}$.

the substance must contain aniline chloride, and this would not have been removed by mere solution in water, the only purification to which it was submitted by Tait. We may add, that the solid matter apparently extracted by ether was really dissolved in the excess of aniline, as it proved insoluble in ether after the aniline was removed, and, as aniline dissolves aniline chloride, we saw no prospect of purifying the phosphorus compound in this way. If, on the other hand, an excess of phosphorus trichloride was used, the product was a white compact mass, from which a considerable amount of solid matter was extracted with ether; but this was due evidently to its solubility in phosphorus trichloride rather than in ether, and, as it contained only two per cent. of phosphorus, it was not thought worth while to pursue this part of the subject further.

Action of Heat on the Original Product.

If the mixture, analyses of which were given above, is heated, it turns orange-red, and gives off aniline chloride, the purity of which was determined by analysis, and a small quantity of a phosphorescent gas, probably phosphoretted hydrogen. This change takes place slowly and partially even at 100° , much more rapidly and completely at 150° , or at even higher temperatures. We usually heated the mass in a porcelain dish over a free flame, regulating the temperature so that aniline chloride sublimed off freely, but no spontaneously inflammable phosphoretted hydrogen was given off. The product when heated with alcohol gave a colorless solution, and a residue of an orange or red color, according to the length of time it had been heated. As this residue was insoluble in all solvents, and could not be purified completely by washing, we are in doubt as to its precise nature; but, as one preparation contained as much as 81.73 per cent. of phosphorus, it cannot be an organic compound, but is either amorphous phosphorus, or the red oxide or solid hydride of that element. The alcoholic solution when treated with water gave a white precipitate of $(\text{C}_6\text{H}_5\text{NH})_2\text{PHO}$, while aniline chloride and phosphite were left in solution, with, so far as we could find, no other substances. The formation of the red body is not essential to the production of the mother-substance of $(\text{C}_6\text{H}_5\text{NH})_2\text{PHO}$, as we obtained, by short heating in a dry test-tube, a yellowish waxy mass, which dissolved completely in alcohol and yielded a large amount of $(\text{C}_6\text{H}_5\text{NH})_2\text{PHO}$ on addition of water; upon longer heating, however, the yellowish substance turned orange-red.

Before going to the description of the phosphorus anilid $(C_6H_5NH)_2PHO$, we may add, that we tried to obtain the chlorine compound from which it is formed by treating the freshly heated orange mass with benzol or with absolute ether, as these solvents seemed to offer the best chance of success. The amount extracted in either case was extremely small, and possessed the most unpromising properties, the ether extract containing lumps of ordinary phosphorus imbedded in a viscous mass, while the benzol extract resembled semi-liquid paint, and gave no evidence that it was a homogeneous compound; it was analysed, however, and contained 5.12 per cent. of chlorine and 21.27 per cent. of phosphorus, whereas $(C_6H_5NH)_2PCl$ requires 14.17 per cent. of chloride and 12.37 of phosphorus.

Phosphorus Anilid, $(C_6H_5NH)_2PHO$.

The preparation of this substance has been just described. In order to purify it, as it did not crystallise, the crude precipitate was redissolved in a little alcohol, and precipitated with water; the viscous mass thus obtained was kneaded thoroughly with water, dissolved again in alcohol, and once more precipitated and washed with water; it was then dried at about 50° , and its composition determined by the following analyses of a number of different preparations:

I. 0.3488 gram of substance gave 0.7992 gram of carbonic dioxide and 0.1918 gram of water.

II. 0.2856 gram gave 0.6502 gram of carbonic dioxide and 0.1610 gram of water.

III. 0.2190 gram gave 0.5012 gram of carbonic dioxide and 0.1180 gram of water.¹

IV. 0.3402 gram gave after treatment, according to Carius, 0.1590 gram of magnesian pyrophosphate.

V. 0.2016 gram gave 0.0976 gram of magnesian pyrophosphate.

VI. 0.4623 gram gave 49.9 cc. of nitrogen at a temperature of 25° and pressure 766 mm.

	Calculated for $(C_6H_5NH)_2PHO$.	I.	II.	III.	Found. IV.	V.	VI.
Carbon	62.07	62.47	62.04	62.41
Hydrogen	5.60	6.10	6.26	5.99
Phosphorus	13.36	13.05	13.52	...
Nitrogen	12.07	12.13

¹ We found it best to carry on the combustions in a closed tube, the substance being mixed with oxide of copper, as, if burnt in a boat in oxygen, the carbon was apt to come low, since the fused phosphoric acid prevented the complete combustion of the substance.

Properties.—It forms a white amorphous mass which melts at 87° ; all our attempts to obtain it in crystals have been unsuccessful; it is freely soluble in cold alcohol and in ether, insoluble in cold water, but melts under boiling water, and perhaps dissolves to a very slight extent. It is a perfectly neutral body, neither acids nor alkalies affecting it in the cold; even alcoholic sodic hydrate or sodic ethylate acts on it with difficulty; on the other hand, fuming hydrochloric acid, when boiled with it for twelve hours, decomposes it completely into aniline chloride, phosphoric acid, and a small quantity of carbonaceous substance. The formation of the aniline chloride was proved by an analysis of the sublimate, 0.2776 gram giving 0.3114 gram of argentic chloride,

	Calculated for $C_6H_5NH_3Cl$.	Found.
Chlorine	27.41	27.74

the formation of phosphoric acid by qualitative tests with argentic nitrate and ammonic molybdate.

Action of Nitric Acid.—When the substance is gently heated with fuming nitric acid it forms a red solution, from which water precipitates a red resinous body which contains phosphorus, but was not studied further, as the quantity was not large, and its properties were uninviting. By far the principal products of the reaction were contained in the aqueous solution, which left on evaporation yellow crystals having acid properties, and easily characterised by their appearance and melting-point, 120° , as picric acid. Another preparation yielded instead of picric acid the unsymmetrical metadinitrophenol, melting at 113° – 115° . These results can be explained by supposing that the nitric acid saponifies the anilid, forming aniline nitrate and phosphoric acid, and the former is afterwards converted into the nitrophenols by the combined action of nitrous and nitric acids.

Action of Acetic Anhydride.—If phosphorus anilid is heated with acetic anhydride and fused sodic acetate on the water-bath, and the product extracted with ether, a viscous mass is obtained, which gradually becomes partially converted into crystals free from phosphorus, melting at 112° after recrystallisation from water, and therefore acetanilid.

From all the observations described above it appears that the substance behaves like an anilid of phosphorus acid.

Action of an Excess of Aniline on the Original Product.

If the immediate product of the action of phosphorus trichloride and aniline, or this product after it has been heated, is boiled for some time with an excess of aniline, there results a mixture of various substances from which we have succeeded in isolating the orange-red substance and phosphorus anilid already described, chloride and phosphite of aniline, and a crystalline substance melting at 208° . There seems to be also a substance with a higher melting-point, and on one occasion a body melting at 150° was obtained; unfortunately we were obliged to break off work on this part of the subject before we had done more than analyse the two substances melting at 208° and 150° respectively, so that we have as yet no satisfactory data for determining their constitution, and also have been able to make no exhaustive search for other products.

Substance melting at 208° .—This compound is obtained from the mixed products of the reaction by washing out the soluble salts with water, extracting the residue with hot alcohol, and purifying the extract by crystallisation from alcohol, till it shows a constant melting-point. It was dried at 100° and analysed.

I. 0.3352 gram gave 0.8032 gram of carbonic dioxide and 0.1770 gram of water.

II. 0.2946 gram gave 0.7047 gram of carbonic dioxide and 0.1520 gram of water.

III. 0.2528 gram gave 0.1200 gram of magnesian pyrophosphate.

IV. 0.2492 gram gave 0.1200 gram of magnesian pyrophosphate.

V. 0.3424 gram gave 40.44 cc. of nitrogen at a temperature of 20.5° and a pressure of 757.3 mm.

	I.	II.	III.	IV.	V.	Mean.
Carbon	65.34	65.24	65.29
Hydrogen	5.86	5.73	5.79
Phosphorus	13.25	13.47	...	13.36
Nitrogen	13.38	13.38

These results agree most nearly with the formula $(C_6H_5NH)_5P_3O_7H_2$, but are not far removed from $(C_6H_5NH)_7P_3O_7H_2$, as is shown by the following comparison:

	Calculated for $(C_6H_5N)_5P_3O_7H_2$.	Mean of analytical results.	Calculated for $(C_6H_5N)_7P_3O_7H_2$.
Carbon	65.61	65.29	65.37
Hydrogen	5.71	5.79	5.70
Phosphorus	14.12	13.36	12.06
Nitrogen	12.75	13.38	12.71

According to the first of these formulas the substance would be a derivative of the red oxide or hydrate of phosphorus, while the second can be developed into $[(C_6H_5NH)_3P]_2H_2O_2PC_6H_5NH$; it is possible, therefore, that a study of the decomposition-products of the substance might throw light on its composition. With this view we heated some of it to 140° in a sealed tube with hydrochloric acid and obtained phosphorus and phosphoric acids, aniline chloride, some carbon, and an odor of phenol, but no red product; we have also found that boiling aniline with the red substance, so often mentioned, does not give this compound melting at 208° , so that our results are in favor of the second formula so far as they go, but need revision before much weight can be given to them.

Properties.—The substance crystallises in small white prisms apparently of the monoclinic system, or in long radiating needles with, as far as we could determine, the same melting-point and composition as the prisms; it melts at 208° , and is insoluble in water, freely soluble in hot alcohol, less so in cold, essentially insoluble in ether. Potassic hydrate in aqueous solution does not act on it at first, but gradually decomposes it if the two are boiled together; sulphuric acid acts in the same way; the decomposition with hydrochloric acid has been described already.

Substance melting at 150° .—This compound was obtained at the very end of the term in an attempt to prepare more of the substance melting at 208° ; on this account we cannot give the conditions which determine its formation, or anything more concerning it than the following analyses:

0.3492 gram of substance gave 0.7122 gram of carbonic dioxide and 0.2004 gram of water.

0.2562 gram gave, according to Carius, 0.1330 gram of argentic chloride and 0.0890 gram of magnesian pyrophosphate.

	Found.
Carbon	55.62
Hydrogen	6.37
Chlorine	12.83
Phosphorus	9.70

It would not be worth while to attempt to determine the formula of this substance until these results have been tested by further analysis. It crystallises in rather thick white radiating needles, melts at 150° , and resembles the preceding substance in a general way in its solubility.

At no distant date we hope to be able to return to the study of this subject in order to determine the nature of the two substances just described, to investigate more thoroughly the products of the reaction, which are soluble in water, and to take up the compounds formed by aniline and phosphorus trichloride in presence of diluents, which, according to a preliminary experiment, promise to be of great interest.

A NEW HYDROUS MANGANOUS ALUMINIC SULPHATE FROM SEVIER CO., TENN.

BY W. G. BROWN.

This mineral, which is found in large quantity at the Alum Cave, Sevier Co., Tenn., was described by Troost in the Geological Survey of Tennessee, and after him by Safford in his *Geology of Tennessee*,¹ as a double sulphate of alumina and potash; and under the head of Kalinite in Dana's *System of Mineralogy*, Alum Cave is given as one of the localities of its occurrence. The Alum Cave is situated at the head-waters of the Little Pigeon, a tributary of the Tennessee River. Called a "cave," it is an overhanging cliff 80 or 100 feet high and about 300 feet long, the top of which projects some twenty or thirty feet beyond the base. In this sheltered ground the "alum" has collected. Hunters who occasionally visit the cave say there is usually a spring flowing. The rock forming the cliff is a weathered schist containing visible specks of pyrite. In the earth produced by the weathering, at the base of the cliff, the alum is found, not on the surface, but covered by a layer of earth and scattered through it in pieces of various sizes. Epsomite is also found in quantity, and Melanterite sparingly at this locality. The "alum" is used by the country people for dyeing their homespun a reddish-brown, and by them preferred to the commercial alum because of the darker red it gives.

The specimen, a portion of which was taken for analysis, consisted of an irregular compact mass, in the cavities of which the

¹ *Geology of Tennessee*, 191, 197, 503.

mineral was found in very fine, transparent needles having a decided silky lustre. An optical examination seemed to indicate that the crystallisation was monoclinic. The compact mineral is white, with a faint tinge of rose, pale green or yellow. Lustre waxy or vitreous. Translucent. On exposure to the air effloresces and becomes coated with a basic salt of iron. Hardness 1.5. Specific gravity, taken in alcohol, 1.782 (average of two pieces respectively 1.775 and 1.790). Heated gently in a closed tube gives off water having an acid reaction. Heated strongly, sulphuric acid is liberated. On platinum before the blowpipe, glows intensely, increases in bulk, and turns reddish-brown. The alumina reaction with cobalt nitrate is obscured by this darkening, but can be obtained by heating in a closed tube. Heated with sodium carbonate on platinum, it gives readily the reaction for manganese. Easily soluble in water. The solution is strongly acid and has a sour, astringent-bitter taste.

The analysis was made by the ordinary methods, except that the water was determined by prolonged heating in a covered platinum crucible (to prevent oxidation of the manganous oxide, which did not take place), in an air-bath, at 220°–240° C. and finally at 300° C. As at this temperature some sulphuric acid was driven off, the dried mass was taken and the amount of sulphuric acid in it determined. The difference between this percentage and that obtained from the air-dry mineral was subtracted from the percentage of loss on heating and the remainder taken as the percentage of water.

The results were as follows:

Al ₂ O ₃	=	10.0318
MnO	=	8.7279
FeO	=	.3874
MgO	=	.2998
(CoNi)O	=	.2948
CuO	=	.0168
SO ₃	=	35.4723
H ₂ O	=	44.7756
Insoluble	=	.0650
		<hr/>
		100.0714

This leads to the general formula

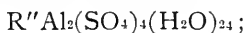


where R'' is principally Mn'', with Fe'', Mg, Co, Ni, and Cu''. This formula, assuming R'' to be Mn'' alone, gives the following calculated composition:

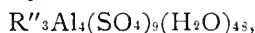
$\text{Al}_2\text{O}_3 =$	9.927
$\text{MnO} =$	10.365
$\text{SO}_3 =$	35.036
$\text{H}_2\text{O} =$	44.672

100.000

A comparison of the composition of this mineral with Apjohnite and Bosjemanite¹ led to a recalculation of the formulae as given in Dana, with the result that the minerals from S. Africa have a composition expressed nearly by the formula



that from Switzerland by



and that from Utah a formula which (in the ratio of H_2O) approaches the Tennessee mineral.

This is shown in the following table, where the compositions and ratios are given, and where the analysis of a "Native Ferrous and Aluminic Sulphate from Tepeji," Mexico,² has been added:

1. Apjohnite, Lagoa Bay, South Africa. Analyst, Apjohn.
2. Bosjemanite, Bosjeman River, South Africa. Analyst, Stromeier.
3. Bosjemanite, Salt Lake, Utah. Analyst, Smith.
4. Bosjemanite, Maderan Valley, Switzerland. Analyst, Schweizer.
- 5.³ Tepeji, Mexico. Analyst, Lippitt.
6. Sevier County, Tenn.

	1.	2.	3.	4.	5.	6.
Al_2O_3	10.65	11.515	10.40	10.55	9.29	10.0318
Fe_2O_3			0.15			
MgO	0.36	3.690	5.94	3.74		.2998
MnO	6.60	2.167	2.12	2.51		8.7279
FeO				1.06	10.03	.3874
$(\text{CoNi})\text{O}$.2948
CuO				0.22		.0168
CaO				0.27		
K_2O			.20	0.58		
KCl		.205				
SO_3	33.51	36.770	35.85	35.96	33.75	35.4723
H_2O	48.15	45.739	46.00	44.26	43.13	44.7756
$\text{CaSO}_4 + 2\text{H}_2\text{O}$					2.24	
	<hr/> 99.27	<hr/> 100.086	<hr/> 100.66	<hr/> 99.15	<hr/> 98.44	<hr/> 100.0064

¹ Dana. A System of Mineralogy. 5th Ed. 1870, 653, 654.

² Lippitt, Chem. News, 48, 98.

³ Changed in form for the sake of comparison.

Ratios.	1.		2.		3.	
Al ₂ O ₃	.104	= 1.02	.112	= 1.00	.101	} .102 = 1.00
Fe ₂ O ₃					.001	
MgO	.009	} .102 = 1.00	.092	} .123 = 1.08	.148	} .18 = 1.76
MnO	.093		.030		.030	
FeO						
(CoNi)O						
CuO						
CaO						
K ₂ O			.001		.002	
SO ₃	.419	= 4.1	.459	= 4.09	.448	= 4.39
H ₂ O	2.675	= 26.22	2.451	= 22.69	2.555	= 25.04

Ratios.	4.		5.		6.	
Al ₂ O ₃	.103	= 1.00	0.91	= 1.00	.098	= 1.00
Fe ₂ O ₃						
MgO	.093	} .157 = 1.53		} .139 = 1.53	.007	} .14 = 1.43
MnO	.035				.123	
FeO	.015				.005	
(CoNi)O					.004	
CuO	.003					
CaO	.005					
K ₂ O	.006					
SO ₃	.449	= 4.35	.422	= 4.63	.443	= 4.51
H ₂ O	2.459	= 23.78	2.396	= 26.33	2.488	= 25.39

These form two well-marked groups:

	Al ₂ O ₃ .	R''O.	SO ₃ .	H ₂ O.	
<i>a.</i>	1.	1.02	1.00	4.10	} R''Al ₂ (SO ₄) ₄ (H ₂ O) ₂₄
	2.	1.00	1.08	4.09	
<i>b.</i>	3.	1.00	1.76	4.39	} R'' ₃ Al ₄ (SO ₄) ₉ (H ₂ O) ₅₁
	4.	1.00	1.53	4.35	
	5.	1.00	1.53	4.63	
	6.	1.00	1.43	4.51	

Neglecting the water, the ratio of R''O to Al₂O₃ is in *a*, 1 : 1; in *b*, 3 : 2.

The two minerals in group *a* differ, in that Apjohnite is a manganous aluminic sulphate, and the African Bosjemanite a manganous magnesian aluminic sulphate.

The minerals in group *b* are of three kinds:

1. Those from Utah and Switzerland are manganous magnesian aluminic sulphates with an excess of magnesia over manganous oxide; this is also the case with the African Bosjemanite.

2. The ferrous aluminic sulphate from Mexico.
3. The manganous aluminic sulphate from Tennessee.

Whether these differences in composition are sufficient to warrant the giving of specific names to these compounds the writer does not feel competent to decide.

UNIVERSITY OF VIRGINIA, *February 7, 1884.*

ON SOME NEW FORMS OF ALBUMOSE.

BY W. KÜHNE AND R. H. CHITTENDEN.

(*Concluded from p. 50.*)

III. *Heteroalbumose.*

During dialysis, particularly of the first protalbumose solution with its abundance of sodium chloride, heteroalbumose separates out in the manner already mentioned, always gummy and thus usually more or less adherent to the sides of the parchment paper, so that frequently even large quantities may be overlooked unless the tubes are cut open. At first the body takes on that turbid, soapy-water-like condition, in the protalbumose solution, so often seen in impure solutions of hemialbumose, and which cannot be removed by filtration; later a syrupy layer forms from this emulsion, which spreads itself out partly in thick lumps and partly as a uniform varnish on the surface of the fluid, appearing as a granular sediment only when in large quantities. By continued withdrawal of the salt all of these forms become more compact and viscous, but only a little more opaque; and the mass, on being scraped out with a spatula and rubbed up with water, still remains transparent, without inclining to separate into flocks. The substance cannot therefore be readily collected on a filter; the fluid is simply decanted and the remainder of the wash-water allowed to drain off by simply inverting the dish. The heteroalbumose then dries in the form of glassy, brittle pieces, not differing in appearance from gelatin tablets, which in the impure condition are tinged with

yellowish or brown and even bright violet, but after purification are as colorless as the purest glass. Unlike gelatin, however, the pieces flake off easily from the glass and porcelain upon which they are dried.

There are two methods of purification: solution in 5-10 per cent. sodium chloride and precipitation with rock salt, re-solution in salt water and dialysis, or simple dialysis of the first filtered salt solution. By the first method there is considerable loss, since the precipitate produced by the salt is not wholly soluble again in dilute salt solutions. The sodium chloride precipitate is gelatinous and elastic, similar to myosin when precipitated by salt. In pure water heteroalbumose is insoluble; the pieces simply become soft and swell up without falling apart, and when the mixture is filtered, even after standing several days, the fluid gives no indications of albumose with the xanthoprotein reaction. A similar result is also obtained when the substance is boiled with water, though the albumose itself becomes more opaque. Sodium chloride solutions from under 0.5 per cent. to saturation dissolve heteroalbumose, quite slowly, it is true, but still in considerable quantity, the best results apparently being obtained with solutions containing from 5 to 10 per cent. of salt. Solutions rich in heteroalbumose are rendered quite turbid by the addition of water. Excess of salt in substance produces an abundant precipitate, as before mentioned, but the separation is never complete, and thus considerable unaltered heteroalbumose can be obtained by the dialysis of the filtrates. Solid heteroalbumose certainly swells up somewhat in water and softens to an almost syrupy mass, without, however, becoming so voluminous as gelatin, for example; when, however, 10 per cent. salt solution is poured over it, heteroalbumose swells up very noticeably and is partially dissolved. If when in this condition pure water is poured over it and the water several times carefully renewed, the very transparent mass contracts and becomes opaque like dull glass.

In addition to neutral salt solutions, dilute acids, alkalies and alkaline carbonates are good solvents for heteroalbumose. Solutions made with the aid of the latter reagents are in general precipitated by neutralisation, never, however, completely, and as a rule the completeness of this precipitation is directly dependent upon the amount of salt formed by neutralisation; the greater the amount of salt the less complete being the precipitation.

Coagulation of Heteroalbumose.

Nothing characterises heteroalbumose more than its alteration by boiling and the properties of the coagulum thus formed. Suspended in water, thereby becoming somewhat swollen, the substance is coagulated by heat after the manner of many undissolved albuminous bodies; for not only do the pieces of the albumose become shrunken and opaque, but they also become wholly insoluble in solutions of sodium chloride of all degrees of concentration. The appearance of the coagulum is quite peculiar; during the heating the substance apparently melts, so that it sticks in strings and patches to the sides of the glass, which after cooling solidify to a resinous or leather-like mass. In solution heteroalbumose likewise coagulates, even in the presence of the weak but still noticeable alkaline reaction which is characteristic of the solution in sodium chloride.

This coagulation is without doubt dependent upon the proportion of the albumose to the sodium chloride used, less so upon the concentration of the salt, for we saw 0.5, 2, 3 and 5 per cent. sodium chloride solutions coagulate by heat with almost equal distinctness, when they were not nearly saturated with albumose; while, on the other hand, when previously diluted with three to five times their volume of sodium chloride solution of like concentration, the solutions would remain perfectly clear on boiling and even afterwards on cooling.

If the proportion is made different, on warming the solution a transitory turbidity is noticed, which by boiling disappears, and on cooling reappears somewhat intensified; on increasing the content of albumose in the solution, the turbidity at 100° C. becomes permanent to such an extent, at least, that the boiling fluid appears milky, and on cooling a slight flocculent precipitate makes its appearance. The hot fluid scarcely passes at all through filter paper, but as the emulsion becomes cool and a flocculent precipitate forms, a quantity of moderately clear fluid filters through sufficient to prove by means of the nitric acid reaction that the coagulation is quite incomplete. Moreover, with the non-coagulated portion of the substance there is as little alteration to be found as in the substance boiled with an excess of salt solution, in which, as before mentioned, there are no appearances whatever of coagulation.

Solutions of heteroalbumose rendered non-coagulable by the presence of a sufficient excess of salt, become by the gradual addi-

tion of acetic acid more and more turbid, until finally they again become clear; a similar reaction is obtained with nitric acid, which, in slight excess, even in the cold colors the solution yellow. Solutions once made clear in this manner by either acetic or nitric acid, remain so on boiling and also on cooling; precipitation however can be produced by the addition of stronger salt solution in the cold, but as the mixture is heated the solution becomes nearly clear, growing turbid again when cold.

Addition of nitric or acetic acid in such quantity that a noticeable turbidity ensues is followed on warming by an increase of the same, which disappears at the boiling point, but returns again considerably increased on cooling.

Properties of Coagulated Heteroalbumose.

We have studied these reactions principally with the substance obtained by boiling heteroalbumose suspended in water, since the substance separating from a salt solution after boiling and then cooling cannot be conveniently collected on a filter, on account of its becoming so finely emulsionised by the melting at 100° C.

Heteroalbumose coagulated by boiling dissolves gradually, but at the same time completely, in hydrochloric acid of from 0.1 to 0.2 per cent., solution being preceded by a swelling up of the substance. It is but very slightly soluble in sodium carbonate of 0.25 to 3.0 per cent., only very faint albumose reactions being obtained in the filtrates with nitric acid. Once dissolved in dilute acids, the coagulum is completely changed, being reconverted in great part into genuine heteroalbumose, while the remaining portion is changed into a substance which agrees perfectly with dysalbumose. Thus the acid solution gives on neutralisation a precipitate which dissolves immediately in dilute sodium carbonate, in part even in sodium chloride of 0.5 to 5.0 per cent., so that precipitation produced in this manner by neutralisation is never complete, owing to the sodium chloride formed. That which remained dissolved in the neutral fluid, together with that which was taken up from the neutralisation precipitate by washing with sodium chloride, behaved in every respect, so far as we could see, like the original heteroalbumose, and which we were able by long-continued dialysis to again separate therefrom; only there was always noticed a portion insoluble in sodium chloride and which was dissolved only by dilute acids or sodium carbonate, the dysalbumose.

That heteroalbumose coagulated from salt solutions does not differ from the coagulum formed by boiling with water is manifest from the continued milkiness of the sample after the addition of sodium carbonate, and also from the clearing up of the fluid by dilute hydrochloric acid, after which alkaline carbonates produce at first a precipitate, which disappears, however, on the addition of an excess of the alkali.

Formation of Albumosat.

If a nearly saturated solution of heteroalbumose in sodium chloride of 3 to 4 per cent. is mixed drop by drop with concentrated hydrochloric acid as long as the precipitate formed at first is dissolved by agitation, or treated in a similar manner with concentrated sodium hydroxide, in which case no precipitation takes place, solutions are obtained which are precipitated by neutralisation after the manner of albuminates. In both cases separation of the precipitate commences a little before the neutralisation point is reached, and appears to be ended when the solution is exactly neutral. The precipitations are, however, never complete, and in comparison with the portion of substance remaining dissolved in the neutral salt solution are quite unimportant.

Boiling genuine heteroalbumose with dilute sodium carbonate or with 0.2 per cent. hydrochloric acid yields solutions of no different proportions than the same solvents give at ordinary temperatures.

Strong acids and alkalies produce on heteroalbumose, to a limited extent, a change similar to the change produced in coagulation, as in the formation of albuminates from undecomposed albumin.

Reactions of Heteroalbumose.

Acetic acid and potassium ferrocyanide produce a heavy turbidity, completely soluble in excess of acetic acid. If a solution of heteroalbumose be mixed with so much acetic acid that the fluid remains clear in the cold, and then a single drop of ferrocyanide be added, which renders the fluid quite turbid, and this followed by the further addition of 20 per cent. acetic acid until the turbidity becomes somewhat lightened, the application of heat then causes the turbidity to almost completely disappear, returning, however, greatly increased as the fluid cools.

With sodium hydroxide and cupric sulphate heteroalbumose gives the so-called biuret reaction; a very slight excess of copper,

however, is sufficient to completely hide this reaction, so that only the blue-violet of the albumin is to be recognised.

By boiling with lead acetate and sodium hydroxide the brown color produced appears less distinct than would be expected from the content of the solution in sulphur-containing material.

Cupric sulphate, neutral and basic lead acetate produce heavy precipitates in the sodium chloride solution of heteroalbumose; the precipitates are insoluble in excess of the reagents.

Towards mercuric chloride heteroalbumose acts very differently than the prot- and dysalbumose, inasmuch as it is not rendered at all turbid even in alkaline, neutralised or faintly acid solutions by either a moderate or excessive addition of the mercury salt. On the addition of acetic acid, however, a heavy precipitate is produced, which is soluble only in a large excess of glacial acetic acid. A solution of heteroalbumose mixed with acetic acid until the solution, at first turbid, has become clear again, is precipitated by an excess of mercuric chloride.

For analysis a preparation (*H*) was used, which had been twice precipitated by dialysis, and while still moist treated with alcohol and ether. When dry it appeared as a fine powder, slightly grey in color.

Heteroalbumose H.

I. 0.5318 gram gave 0.3167 gram $H_2O = 6.61$ per cent. H and 0.9790 gram $CO_2 = 50.20$ per cent. C.

II. 0.7977 gram gave 0.4760 gram $H_2O = 6.63$ per cent. H and 1.4700 grams $CO_2 = 50.25$ per cent. C.

III. 0.5731 gram gave 0.3473 gram $H_2O = 6.73$ per cent. H and 1.0598 grams $CO_2 = 50.42$ per cent. C.

IV. 0.5113 gram gave 73.92 cc. N at $19.2^\circ C.$ and 761.6 mm. pressure $= 0.0869289$ gram N $= 17.00$ per cent.

V. 0.5407 gram gave 77.93 cc. N at $19.9^\circ C.$ and 765.37 mm. pressure $= 0.0918370$ gram N $= 16.98$ per cent.

VI. 0.4545 gram gave 0.0041 gram ash $= 0.90$ per cent.

VII. 0.7010 gram gave 0.0064 gram ash $= 0.91$ per cent.

The ash was composed entirely of gypsum.

The ash from 1.1555 grams substance gave 0.0033 gram $BaSO_4 = 0.03$ per cent. S, contained in the original substance as gypsum.

VIII. 0.5448 gram substance gave after the nitrate fusion 0.0472 gram $BaSO_4 = 1.18$ per cent. S; deducting 0.03 per cent. $= 1.15$ per cent. S.

IX. 0.3085 gram gave after the nitrate fusion 0.0265 gram BaSO_4 = 1.17 per cent. S; deducting 0.03 per cent. = 1.14 per cent. S.

Percentage composition of ash-free heteroalbumose *II*:

								Average.
C	50.64	50.70	50.88	50.74
H	6.67	6.69	6.79	6.72
N	17.15	17.13	17.14
S	1.17	1.16	1.16
O	24.24

To obtain the specific rotary power, 0.9700 gram dry substance = 0.9613 gram ash-free substance was dissolved in 35 cc. H_2O + 20 cc. 0.2 per cent. HCl , in which 1 cc. contained 0.017478 gram pure substance. As a mean of 3 observations the solution in a 100 mm. tube rotated the light 1.2° to the left, therefore,

$$(\alpha)_D = \frac{1.2^\circ}{0.017478 \cdot 1} = -68.65^\circ.$$

IV. *Dysalbumose*.

This body is obtained by careful extraction of the insoluble residue remaining from the treatment of Witte's "pepton" with salt solution. The residue is first extracted with saturated, then with 10 and 5 per cent. salt solutions, and finally with water. It is then treated with 0.2 per cent. hydrochloric acid, by which nearly all is dissolved, filtered, and the filtrate made exactly neutral. So large a portion has now become soluble in sodium chloride that by dialysis of the filtrate, together with the wash fluid which at first consisted of 5 per cent. sodium chloride, a considerable quantity of albumose is obtained, which behaves exactly like heteroalbumose. The portion not changed into heteroalbumose is, after thorough washing with sodium chloride and water, for which purpose it is repeatedly rubbed up fine, extracted with alcohol and ether.

Analysis of the so-obtained light grey powder (preparation *J*) gave the following results:

Dysalbumose J.

I. 0.5086 gram gave 0.3141 gram H_2O = 6.86 per cent. H and 0.9384 gram CO_2 = 50.31 per cent. C.

II. 0.5438 gram gave 0.3299 gram H_2O = 6.73 per cent. H and 0.9997 gram CO_2 = 50.13 per cent. C.

III. 0.4068 gram gave 0.2500 gram H_2O = 6.83 per cent. H and 0.7501 gram CO_2 = 50.28 per cent. C.

IV. 0.4437 gram gave 62.93 cc. N at 18.6°C . and 768.21 mm. pressure = 0.0748023 gram N = 16.86 per cent.

V. 0.6524 gram gave 94.16 cc. N at 19.6°C . and 758.4 mm. pressure = 0.1101142 gram N = 16.87 per cent.

VI. 0.6914 gram gave 0.0088 gram ash = 1.27 per cent.

VII. 0.7030 gram gave 0.0090 gram ash = 1.28 per cent.

The ash contained no carbonic acid, only some ferric oxide and calcium sulphate.

The ash from 1.3944 grams substance gave 0.0031 gram BaSO_4 = 0.03 per cent. S, in the original substance in the form of sulphate.

VIII. 0.5400 gram substance gave by the nitrate fusion 0.0509 gram BaSO_4 = 1.29 per cent. S; deducting 0.03 per cent. = 1.26 per cent. S.

IX. 0.5480 gram gave after the nitrate fusion 0.0480 gram BaSO_4 = 1.20 per cent. S; deducting 0.03 per cent. = 1.17 per cent. S.

Percentage composition of ash-free dysalbumose J:

								Average.
C	50.95	50.77	50.92	50.88
H	6.95	6.82	6.92	6.89
N	17.07	17.08	17.08
S	1.28	1.19	1.23
O	23.92

The specific rotary power could not be satisfactorily determined, owing to the deep color of the solution.

Dysalbumose, as is plainly seen, does not differ materially in composition from the other forms of albumose, certainly not more than these differ from each other; while, like the other forms of albumose, it differs very decidedly from the albumins, syntonins, etc.; which fact is alone sufficient to remove the suspicion that the substance belongs to a residue of non-separated neutralisation precipitate (Meissners), or the so-called digestion syntonin. Further, this idea is completely overthrown by the ready conversion of our preparation into heteroalbumose. It is only necessary to dissolve some of it in 1 per cent. sodium carbonate, when on neutralisation it

will be found (with the exception of a hardly noticeable residue) quite soluble in sodium chloride, and can then be easily obtained by dialysis, with all the properties of heteroalbumose. We therefore consider dysalbumose simply as a form of heteroalbumose, which has become insoluble in neutral salt solution, and thus its origin, by treatment of the digestive solutions with salt, is readily comprehended, since pure heteroalbumose cannot be precipitated by salt without being partially converted into a substance not distinguishable from dysalbumose. Heteroalbumose likewise suffers the same change by long preservation under alcohol or in a dry condition; for the preparations, at first completely soluble in sodium chloride, become after a time more or less insoluble, so that a residue remains which at the best forms with salt water only a milky emulsion.

As to the reactions of dysalbumose, it is only necessary to refer to heteroalbumose, since in both acid and alkaline solutions of the former we found nothing characteristic, other than the solubility of the nitric acid precipitates by heat and their reappearance on cooling; with dysalbumose which had become soluble in salt solutions, no other reactions were observed than those described under heteroalbumose.

While the several forms of albumose just described are seen to differ somewhat in their general properties, the percentage composition of the various products shows a remarkable degree of uniformity. This close agreement in composition, which is plainly apparent from the following table, is probably due in great part to the purity of our preparations, which were not only carefully prepared, but were made in large quantities, thus admitting of even lavish purification. In the table the averages of the individual analyses are given, calculated on the ash-free substance, while for the sake of comparison the content of ash is given, also the specific rotary power¹ as determined in very dilute hydrochloric acid solutions (under 0.1 per cent.).

¹ The figures for specific rotary power agree with the statement of Salkowski (*loc. cit.* p. 213), "about -75° " for the aqueous solution of his substance, which probably consisted mainly of prot- and deuterioalbumose.

	Protalbumose.			Protalbumose. NaCl P.P. Acid P. P.		Deuteroalbumose.		Hetero- albumose.	Dys- albumose.
	A.	B.	C.	D.	E.	F.	G.	H.	I.
C	50.89	50.39	50.54	51.50	50.55	50.47	50.84	50.74	50.88
H	6.83	6.74	6.69	6.80	6.85	6.81	6.85	6.72	6.89
N	17.12	17.12	17.34	17.13	17.01	17.20	17.14	17.14	17.08
S	1.17	1.07	1.17	0.94	1.07	0.87	1.07	1.16	1.23
O	23.99	24.68	24.26	23.63	24.52	24.65	24.10	24.24	23.92
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ash	0.90	0.22	2.58	1.60	1.32	1.77	0.68	0.90	1.27
(a) _p	-72.64°	-79.05°	-77.90°	-73.18°	-71.40°	-74.41°	-79.11°	-68.65°	...

V. *Albumose in Urine in Osteomalachia.*

Of this substance we had for examination only a small residue of the dry, preserved material precipitated by alcohol from the urine of a patient with the above disease, a description of which was given in our previous article.¹ In spite of the rarity of the object it seemed worth the labor to use some of the substance for the purpose of comparison with the above forms of albumose.

2.5 grams were ground fine with 50 cc. of water and then allowed to stand for several days without warming, a little thymol being added to prevent decomposition. Crystals of salt added to the clear acid filtrate produced a heavy precipitate, also when added to the neutralised or faintly alkaline (with sodium carbonate) solution. In a solution made quite strongly alkaline, however, the salt produced more of a turbidity than a compact flocculent precipitate. The entire solution of the substance precipitated with salt and filtered was not at all affected by dilution with a large quantity of saturated salt solution. With nitric and acetic acid, however, the solution was rendered somewhat turbid; excess of acetic acid rendered the solution clear again. The precipitates formed by these two acids were quite small, especially in comparison with the first precipitate produced by salt alone. The salt precipitate, pressed on the filter, dissolved in water and separated a second time by trituration with an excess of sodium chloride, again yielded a filtrate, precipitable by both nitric and acetic acid. Thus the agreement with protalbumose is quite evident. Certain detection of deuteroalbumose, which was probably also present, had to be given up on account of the small amount of material.

¹ Zeitschrift für Biologie, 19, 159, also 19, 209.

As the preserved urine-albumose was in great part insoluble in water, and as this insoluble portion melted by boiling in exactly the same manner as hetero- and dysalbumose, becoming emulsified and afterwards hardening to a leather-like mass, we thought it best to examine the residue remaining after thorough washing with cold water, for these two forms of albumose. This residue, as reported in the previous publication, gave up something to 5 per cent. sodium chloride, which showed the general reactions of hemialbumose. This we found to be the case also in the present instance. The amount of substance dissolved, however, was too small, even from 5 grams of fresh material, to identify it with certainty as heteroalbumose, which can be conveniently done only through its separation by long-continued dialysis.

The residue remaining after treatment with salt solution was scarcely at all diminished in bulk, and was more than sufficient to furnish proof that it consisted of dysalbumose. This was plainly demonstrated by the fact that after complete extraction with water the residue dissolved almost completely both in 0.2 per cent. hydrochloric acid and in 2.5 per cent. sodium carbonate in $\frac{1}{2}$ -1 hour *without warming*. On neutralisation the substance was only partially precipitated; a portion of the precipitate was soluble in 5 per cent. sodium chloride. That portion of the neutralisation precipitate insoluble in sodium chloride can be considered as unaltered dysalbumose, while the portion taken up by the salt solution was naturally to be considered as converted into heteroalbumose.

Contrary to all expectation, however, the salt solution did not act like a solution containing heteroalbumose; it was only rendered slightly turbid by crystals of salt, while the filtrate gave an abundant precipitate on the addition of acetic acid containing salt. Heteroalbumose obtained by digestion, on the contrary, is readily precipitated by solid salt, and although never completely, it separates to such an extent that the addition of acetic acid afterwards produces only a strong opalescence. The principal difference, however, consisted in the fact that the united solutions after two days dialysis, at which time every trace of chlorine had disappeared, showed hardly any trace of turbidity, and nothing had apparently been deposited on the walls of the parchment tubes. In this purified condition the clear filtered solution of slight alkaline reaction gave a heavy coagulum by warming, without becoming in the least transparent on boiling. The solution was likewise precipitated in

the cold by nitric acid, which even in great excess did not produce a complete clearing of the solution, but left a large residue of yellow flocks.

Possible contamination with ordinary albumin might seem at first as the probable explanation of this appearance, but this was shown not to be the case by the ordinary hemialbumose reaction, since the substance precipitated in the cold by nitric acid dissolved on warming even in the slightest excess of acid and re-appeared on cooling.

The present investigation was begun in the hope of finding a satisfactory explanation for the very changeable behavior of the solutions and precipitate obtained in the primary digestive or other albuminous cleavage processes. It is our intention to continue our work in this direction. The first steps would appear now to have been accomplished since we have succeeded: 1st, in proving the existence of a row of bodies between albumins and peptones, the composition of which points to a gradual course of hydrolytic decomposition, and thus these forms of albumose are to be considered collectively as the first hydrates; 2d, in obtaining proof that the different forms of albumose not only fall apart into the anti- and hemi-group, but that now the hemi-group by itself can be considered as consisting of several members. According to all appearances also, this holds good not only for the cleavage products of fibrin, but also for those of albumin, myosin, etc., since we have frequently obtained after the digestion of such material, by the methods described in this paper, many products which at least are very similar to those described here.

Moreover, we are now in a position to explain the earlier found fact concerning "soluble" and "insoluble" albumose, as well as the contradiction regarding the precipitability of albumose, in part by sodium chloride alone and in part only by the united action of an acid.

What was previously designated "insoluble" hemialbumose consists of heteroalbumose, soluble only in boiling dilute sodium chloride, and which after once being boiled separates out in great part on cooling. "Soluble" hemialbumose corresponds to both protalbumose and deuterioalbumose, or to a mixture of both of these bodies. When protalbumose is obtained free from deuterioalbumose, it is at once evident, from the fact that the latter cannot

be precipitated by sodium chloride alone; but since we have become familiar with heteroalbumose, it is also clear that in the majority of cases the precipitate obtained by simple addition of sodium chloride cannot be pure protalbumose, as there remains mixed with it a portion of heteroalbumose which can be separated by dialysis. On the other hand, it is less clear how a complete separation of deutoalbumose from protalbumose is accomplished; for while it is a very easy matter to obtain the latter free from the first, the reverse, it would appear, must be correspondingly difficult, because the purified protalbumose is never completely separated by simple addition of salt, but is largely precipitated together with deutoalbumose by the subsequent addition of acid. It would thus appear that deutoalbumose can only be obtained contaminated with protalbumose. Yet, the above-described method of treatment of the commercial albumose mixture has furnished us the body so pure that its neutral solution was not made at all turbid by solid sodium chloride, a pleasant circumstance, which afterwards astonished us the more when we found that with our present means it is impossible to obtain the body pure again when it is mixed with ever so pure a solution of protalbumose. Probably the peculiar intermingling of protalbumose with hetero- and dysalbumose as found in Witte's preparation, is the reason of the complete insolubility of the former when the powder is at first treated with solid sodium chloride and salt solution, so that then deutoalbumose goes into solution at the outset quite free from its obstinate companion.

The earlier statements regarding the turbidity and precipitation of hemialbumose by neutralisation, as also its precipitation, after the manner of albuminates, from solutions originally non-precipitable after their solutions have been treated with caustic alkalies or strong acids, find their explanation in the properties of hetero- and dysalbumose already described. It is hardly necessary to mention that such appearances can be observed in the case of prot- and deutoalbumose, only when extraordinarily concentrated solutions or solutions rich in salt are used.

A comparison of the analytical results obtained from the separate forms of albumose with those obtained earlier,¹ shows the closest agreement in the majority of cases; thus, "soluble hemialbumose *B*" from fibrin was composed of C 50.40, H 6.69, and

¹ Compare *Zeitschrift für Biologie*, 19, 193.

N 17.37 per cent. On the other hand, a very noticeable difference is found in the composition of the albumose from urine, which contained C 52.13, H 6.83, and N 16.55 per cent., and thus agrees the least in composition with the remaining samples of hemi-albumose obtained from the earlier preparations from both albumin and fibrin. We surmise that the reason of this, as well as of the other difference noticed in testing for heteroalbumose, is to be found in the origin of the urine albumose. The nature of the albuminous matter from which it originated is too little known, and on the same grounds we consider it very desirable that the forms of albumose of all of the albuminous bodies, viz. of serum-albumin, globulin, myosin, etc., should be investigated in the same manner as those of fibrin.

That we have in the present article explained all and each of the remarkable reactions which are to be observed in the digestive mixtures of albuminous matter we do not once imagine; thus, we still remain in doubt as to the reason of the paradoxical appearance recently noticed in the digestive mixture containing albumose (freed from neutralisation precipitate), where the solution containing a certain amount of salt is plainly coagulated by boiling only to become clear again on cooling; a most complete reversal of the most general of all albumose reactions.

We deemed it of considerable interest to see whether there were among the new-found bodies any which did not belong to the hemi-group. In our search after a pure hemialbumose which should be *completely* decomposed by trypsin, that is to say converted into amido-acids, etc., without a trace of peptone or albuminous body remaining, we have perhaps pursued a phantom. The experiment, however, was needed to discover whether or not there was concealed in the hemialbumose a residue of the anti-group. To this question a positive answer was at once obtained, for it was found that both hetero- and dysalbumose do not belong exclusively to the hemi-group. Originally of the opinion that these bodies would fill up the gap in the scheme of albumin cleavage previously devised by one of us, and that a hemialbumat would be revealed, we must now, after the results of the analyses which have given much too low percentages of carbon for the conjectured anhydride, turn our attention to some other view.

Of all the primary cleavage products, antialbumose is, up to the present, the most difficult to obtain, and at the same time is the

least known. That this product is represented by a single body is, after the new experiences with hemialbumose, hardly to be supposed, and thus the possibility is suggested that a portion of the constituents of which hemialbumose is now known to be composed, constitute in part antialbumose. Trypsin digestion was employed as a means of determining this point. The digestion was made first of all with prot- and deuteroalbumose, partially in aqueous solution and in part with the addition of one per cent. sodium carbonate, and certainly so large an amount of leucin, tyrosin, as well as the body colored violet by bromine, together with so small an amount of peptone, was never obtained from any of the earlier preparations of hemialbumose. These experiments, on account of the difficulty of preparing peptone-free trypsin, are not yet completely finished, and not yet decisive as to the complete removal of all matter of the anti-group from these two bodies. On the other hand, we can say with certainty from the first experiments with heteroalbumose, that this substance contains bodies of the anti-group, for we obtained from it by the action of trypsin non-decomposable *antialbumat*, changeable only into peptone.

Four grams of colorless glassy heteroalbumose, coming from a fibrin-pepsin digestion and twice purified, were dissolved in 200 cc. of 0.5 per cent. sodium carbonate, and warmed at 40° C. with about 1 gram of purified trypsin. The trypsin was not entirely free from peptone, but contained no trace of leucin, tyrosin, or other crystalline body, and a concentrated solution gave no color whatever with bromine water. After two hours the clear digestive mixture began to grow turbid, and at the end of six hours this turbidity had increased to a semi-gelatinous coagulation, which had all the appearances of the albumid coagulum. After filtration from this precipitate the fluid did not become turbid again by further warming at 40° C., neither was it rendered turbid by neutralisation nor by slightly acidifying. Evaporated and then extracted with alcohol it gave the usual peptone precipitate, coming in part without doubt from the trypsin, together with a crystalline deposit of leucin and tyrosin; moreover, a much more intense violet bromine reaction was obtained than would ordinarily be expected from the small amount of amido acids present. Bodies of the hemi-group are therefore contained in the heteroalbumose, and since it is evident both from the composition and reactions of the latter that undecomposed

albumin cannot be the cause of its peculiarities, it must therefore be a mixture, probably of hemi- and antiheteroalbumose.

The coagulum produced by trypsin was easily proved to be antialbumat, for on being dissolved in 0.2 per cent hydrochloric acid and mixed with very active purified gastric juice which gave no precipitate itself on neutralisation, and kept at 40° C. for 48 hours, it separated out on neutralisation apparently not at all diminished in amount; it was thus non-digestible in gastric juice. Warmed again with sodium carbonate, this time in a 1 per cent. solution, and then mixed with trypsin, the body separated from the solution a second time, although in smaller quantity than at first; and finally after 5 days continued digestion, with gradual addition of sodium carbonate until the mixture contained fully 3 per cent. of alkali, we succeeded in bringing it wholly into solution with the exception of a slight turbidity. After filtration through paper the fluid then remained unaltered during 8 days longer digestion. Neutralised with acetic acid the fluid gave no precipitate whatever, and in spite of the most careful and repeated treatment with alcohol nothing was found in the fluid other than peptone (antipeptone); not even a trace of leucin or tyrosin was to be detected, and with bromine water no indications of a violet or rose color. Thus the product separated as a coagulum by trypsin was found to be soluble and digestible in the presence of a sufficient amount of alkali, but like bodies of the anti-group was only convertible into peptone, not decomposable by the digestive mixture.

At the conclusion of this experiment another test was tried directly with heteroalbumose obtained from Witte's preparation; that is to say, the preparation without previous conversion into the albumat was treated with gastric juice, in order to see whether the supposed antiheteroalbumose is so difficultly or so slowly digestible in pepsin as is known to be the case with antialbumose in general. 4 grams of the substance were dissolved in 200 cc. 0.2 per cent. hydrochloric acid, and then mixed with an equal quantity of pure dialysed gastric juice of the same degree of acidity. A small portion of the mixture dissolved a piece of fibrin completely in five minutes, the fluid was therefore active. After eighteen hours warming at 40° C. it appeared, judging from the heavy neutralisation precipitate obtained in a portion tested, hardly at all digested, and not until the mixture had been warmed for five days was the heavy flocculent neutralisation precipitate obtained in a portion with-

drawn from the mixture, replaced by a turbidity. But even then when the entire quantity was neutralised an almost resinous precipitate was obtained, while in the filtrate a heavy turbidity was produced by sodium chloride and nitric acid, which disappeared on the application of heat, reappearing again as the solution cooled; a reaction naturally to be referred to the incomplete precipitation of heteroalbumose by neutralisation.

We cannot but think that dysalbumose, coming as it does from heteroalbumose, will show a similar behavior towards pepsin and trypsin digestion, and we hope in the near future to demonstrate this, as well as several other suppositions, by a continuation of our present line of work.

Addenda.

In order to obtain further knowledge of the rotary power of these forms of albumose, we have, since the above was written, made in addition to the observations in dilute acid solutions already described, several experiments, both in faintly alkaline solutions and in sodium chloride solutions, with the following results:

Protalbumose A.

1.1088 grams previously dried at $105^{\circ}\text{C.} = 1.0989$ grams ash-free substance dissolved in 40 cc. $\text{H}_2\text{O} + 10$ cc. 0.6 per cent. $\text{Na}_2\text{CO}_3 = 0.021978$ gram substance per cubic centimetre, gave with the fluid at 20°C. :

In 200 mm. tube as a mean of 4 observations $- 3.55^{\circ}$ rotation, therefore $(\alpha)_D = - 80.76^{\circ}$;

In 220 mm. tube as a mean of 4 observations $- 3.95^{\circ}$, therefore $(\alpha)_D = - 81.69^{\circ}$.

Protalbumose B.

1.1362 grams $= 1.1337$ grams ash-free substance in 41 cc. $\text{H}_2\text{O} + 10$ cc. 0.6 per cent. $\text{Na}_2\text{CO}_3 = 0.022229$ gram per cubic centimetre, gave at 21°C. :

In 200 mm. tube as a mean of 5 observations $- 3.12^{\circ}$, therefore $(\alpha)_D = - 70.17^{\circ}$;

In 220 mm. tube as a mean of 7 observations $- 3.54^{\circ}$, therefore $(\alpha)_D = - 70.93^{\circ}$.

Protalbumose C.

I. 0.9610 gram = 0.9363 gram ash-free substance in 40 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 = 0.018726 gram per cubic centimetre, gave with the solution at $23.5^\circ \text{C}.$:

In 200 mm. tube as a mean of 7 observations — 3.0° , therefore $(a)_D = -80.10^\circ$;

In 220 mm. tube as a mean of 8 observations — 3.3° , therefore $(a)_D = -80.10^\circ$.

II. 1.2115 grams = 1.1803 grams ash-free substance in 40 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 = 0.023606 gram per cubic centimetre, gave at $22.5^\circ \text{C}.$:

In 200 mm. tube as a mean of 5 observations — 3.74° , therefore $(a)_D = -79.21^\circ$;

In 220 mm. tube as a mean of 8 observations — 4.11° , therefore $(a)_D = -79.14^\circ$.

Protalbumose D.

0.7490 gram = 0.7411 gram ash-free substance in 40 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 = 0.014822 gram per cubic centimetre, gave with the solution at $21^\circ \text{C}.$:

In a 200 mm. tube as a mean of 7 observations, a rotation of -2.1° , therefore $(a)_D = -70.84^\circ$.

Protalbumose E.

I. 0.9645 gram = 0.9518 gram ash-free substance in 40 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 = 0.019036 gram per cubic centimetre, rotated the light with the temperature of the fluid $24.5^\circ \text{C}.$:

In 200 mm. tube as a mean of 6 observations — 2.90° , therefore $(a)_D = -76.17^\circ$;

In 220 mm. tube as a mean of 6 observations — 3.20° , therefore $(a)_D = -76.41^\circ$.

II. 1.2637 grams = 1.2471 grams ash-free substance in 40 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 = 0.024942 gram per cubic centimetre, rotated the light with the fluid at $24.5^\circ \text{C}.$:

In 200 mm. tube as a mean of 8 observations — 3.79° , therefore $(a)_D = -75.97^\circ$;

In 220 mm. tube as a mean of 8 observations — 4.10° , therefore $(a)_D = -74.72^\circ$.

Deuteroalbumose F.

I. 1.4205 grams = 1.3954 grams ash-free substance in 45 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 = 0.0253709 gram per cubic centimetre, rotated the light with the solution at $23^\circ \text{C}.$:

In 200 mm. tube as a mean of 8 observations — 3.77° , therefore $(a)_D = -74.29^\circ$;

In 220 mm. tube as a mean of 8 observations — 4.33° , therefore $(a)_D = -77.57^\circ$.

II. 0.6549 gram = 0.6434 gram ash-free substance dissolved in 50 cc. 0.5 per cent. NaCl = 0.012868 gram per cubic centimetre, rotated the light with the solution at $22^\circ \text{C}.$:

In 200 mm. tube as a mean of 5 observations — 2.0° , therefore $(a)_D = -77.71^\circ$;

In 220 mm. tube as a mean of 6 observations — 2.18° , therefore $(a)_D = -77.00^\circ$.

Deuteroalbumose G.

I. 0.9065 gram = 0.9004 gram ash-free substance in 41 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 = 0.0176549 gram per cubic centimetre, rotated the light, the solution at a temperature of $22.5^\circ \text{C}.$:

In 200 mm. tube as a mean of 6 observations — 2.68° , therefore $(a)_D = -75.90^\circ$;

In 220 mm. tube as a mean of 6 observations — 2.90° , therefore $(a)_D = -74.66^\circ$.

II. 1.0419 grams = 1.0349 grams ash-free substance in 54 cc. 0.5 per cent. NaCl = 0.0191648 gram per cubic centimetre, rotated the light with the solution at $22^\circ \text{C}.$:

In 200 mm. tube as a mean of 7 observations — 2.73° , therefore $(a)_D = -71.22^\circ$;

In 220 mm. tube as a mean of 7 observations — 3.07° , therefore $(a)_D = -72.81^\circ$.

Heteroalbumose H.

0.8154 gram = 0.8081 gram ash-free substance was dissolved in 36 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 + 5 cc. 2 per cent. Na_2CO_3 (a clear solution was not obtained until the addition of the stronger solution of alkali) = 0.015845 gram per cubic centimetre. On account of the opalescence of the solution it was examined only in a 100 mm. tube, and with the solution at $20^\circ \text{C}.$ it rotated the light as a mean of 7 observations — 0.96° , therefore $(a)_D = -60.58^\circ$.

The average results obtained in both acid and alkaline solutions are represented for the sake of comparison in the following table:

	PROTALBUMOSE.			PROTALBUMOSE.		DEUTEROALBUMOSE.		HETEROALBUMOSE.	
	A.	B.	C.	NaCl Precip. D.	Acid Precip. E.	F.	G.		
Acid solution.....	-72.64°	-79.05°	-77.00°	-73.18°	-71.40°	-74.41°	-79.11°	-68.65°	} (a) _n
Alkaline solution..	-81.22°	-70.55°	-79.64°	-70.84°	-75.82°	-75.93°	-75.28°	-60.65°	
NaCl solution.....	-75.35°	-71.96°	..	

REVIEWS AND REPORTS.

THE ARTIFICIAL PREPARATION OF OPTICALLY ACTIVE SUBSTANCES.

Chemists generally assume that all chemical substances can be made in the laboratory by artificial methods, and certainly when we consider the many syntheses of natural substances that have been effected during the last thirty years, the assumption appears to be justified. Nevertheless, there are some facts which speak against it. Several of the vegetable acids have the power of turning the plane of polarised light either to the right or left. Some of these substances have been prepared artificially, and the products thus obtained have been shown to have all the properties of the corresponding natural substances with the exception of the optical activity. Thus natural malic acid is laevo-rotatory, while the malic acid obtained from brom-succinic acid is optically inactive. Such facts have led gradually to the conclusion that artificially prepared substances cannot act upon polarised light, that in order to get an optically active substance we must have the intervention of the life process.

Finally, however, Perkin and Duppa succeeded in making racemic acid from bibrom-succinic acid, and Jungfleisch and Pasteur showed that this artificially prepared racemic acid could be split up into dextro- and laevo-tartaric acids. Thus the artificial preparation of one optically active substance was certainly accomplished, and, while some chemists concluded that the same result would probably in time be reached in connection with all optically active substances, others preferred to suspend judgment and await further developments.

Last December, M. Pasteur, in a lecture¹ before the Paris Chemical Society, called special attention to the subject. The lecture has given rise to an interesting discussion between MM. Wyruboff, Jungfleisch and Pasteur, the substance of which, together with two papers on the subject by M. Jungfleisch, are published in the Bulletin de la Société Chimique de Paris, Vol. 41, No. 5 (March 5, 1884). In view of the interest which the subject must have for all chemists, abstracts of M. Pasteur's lecture and the other papers referred to are here given. M. Pasteur began his lecture by describing in detail the crystallisation of the double racemate of ammonium and sodium, and the formation of the two kinds of crystals from it. To use his own words: "A new idea soon occurred to me. These crystals, asymmetric to the right, which I could separate mechanically from the others, proved to be identical in form with those of the dextro-tartrate. . . I separated these right-handed crystals from the crystallised racemate; I made the lead salt and isolated the acid. This acid was absolutely identical with the tartaric acid from grapes, and, like it, acted upon polarised light. I was still happier when, on taking in turn the left-handed crystals obtained from the racemate, I obtained a tartaric acid quite similar to ordinary tartaric acid, but having a form asymmetrical in the opposite way, and acting in the opposite direction upon polarised light. The form was identical with that of the image of dextro-tartaric acid placed before a mirror. The principles of '*molecular asymmetry*' were thus founded. There are substances of which the atomic grouping is asymmetrical, and this grouping shows itself in an asymmetric form and in an action upon polarised light; besides, these atomic groupings have their possible complements, the forms of which are identical with the images of the first, and with an opposite action upon polarised light. . . .

"Now, gentlemen, there is one strange peculiarity about this molecular asymmetry. We find asymmetry established in a very large number of the proximate principles of animals and vegetables, notably in the proximate principles essential to life. All the products, so to speak, of the egg and the seed are asymmetrical.

"There are, without doubt, in animals and vegetables proximate principles, such as urea and oxalic acid, which are not asymmetrical; but these are secondary products, comparable in one sense to our laboratory products, which are not asymmetrical.

"In other words, when a ray of sunlight strikes a green leaf, when the carbon of carbonic acid, the hydrogen of water, the nitrogen of ammonia, and the oxygen of the carbonic acid and of the water form chemical compounds, and the plant grows, the bodies which are thus developed are asymmetrical. You, however, skillful chemists as you are, though you bring together the same elements in a thousand different ways, always make products without

¹ Revue Scientifique, Jan. 5, 1884.

molecular asymmetry. As far as I know, there does not exist a single product of chemical synthesis, formed under the influence of causes which may be considered peculiar to vegetable life, which is not asymmetrical. . . . On the other hand, there is not a single product of synthesis prepared in the laboratory or in dead mineral nature, which is not symmetrical."

The speaker then referred to the synthesis of racemic acid from bibrom-succinic acid, and the splitting up of this artificial product into dextro- and laevo-rotatory tartaric acids. He denied that this synthesis disproved his statement that optically active substances cannot be prepared synthetically. He quoted the words of Le Bel, as follows: "It is then not only vegetable life which includes cases of asymmetry, and the line of demarcation between vegetable and mineral chemistry pointed out by M. Pasteur does not exist." To this he remarked: "That is an error. I claim to be able to show you that this separation, this barrier, is on the contrary confirmed by the results first observed by myself, and afterwards by M. Jungfleisch and by M. Le Bel.

"We can explain the facts regarding asymmetry in the following manner: When the proximate principles which are essential to life are formed, it is under the influence of asymmetrical forces, and that is why life produces asymmetrical substances. When the chemist in his laboratory combines the elements or compounds formed from the elements, he does not bring into play the asymmetrical forces. That is why all the substances which he produces by synthesis are devoid of asymmetry. . . . You ask: what then are the asymmetrical forces which preside over the elaboration of the proximate principles of nature? It would be difficult for me to answer with accuracy; but asymmetry I see everywhere in the universe. The universe is asymmetrical. . . . You in your laboratories, with your solvents, your heat and cold, have at your service only symmetrical forces. Is there then an absolute division? Certainly not. Far from saying or thinking so, I first pointed out the means which we might make use of to destroy the barrier. What must we do to imitate nature? We must break loose from our methods, which are from this point of view antiquated and impotent. We must try to bring into action the asymmetrical forces, we must have recourse to the action of the solenoid, of magnetism, of the asymmetrical motion of light, to the action of substances which are themselves asymmetrical. When, carried away by inexorable logic, I passed from researches in crystallography and molecular chemistry to the study of ferments, my thought was to introduce asymmetry into chemical phenomena. . . . On bringing together cinchonine, an active asymmetrical substance, and racemic acid, I saw the cinchonine salt of laevo-tartaric acid deposited, while the dextro-tartrate remained in solution. With an inactive body, racemic acid, I have made laevo- and dextro-tartaric acids. Although I was the first to imitate nature in its methods, and to show the analogy between natural

and artificial products, I am careful not to conclude that the barrier between the two chemistries is destroyed. On the contrary, I conclude that the experiment of which I have spoken establishes the proposition, namely, that the forces brought into play in our laboratories differ from those to which vegetable nature is subject.

"In another way, much more interesting, I have introduced asymmetry into chemical actions. I have shown that ammonium racemate can ferment under the influence of microscopic fungi, and that laevo-tartaric acid appears. The dextro-tartrate is decomposed, the laevo-tartrate remains intact. With an inactive racemate I have caused the appearance of simple asymmetry, but why? Because the little ferment is a living body formed of a collection of asymmetrical products, and because for purposes of nutrition the little being finds the dextro-tartrate better adapted than the laevo-tartrate.

"I have gone further: I have caused to grow on the surface of ashes and racemic acid, some grains of *Penicillium glaucum*, that mould which is found everywhere, and I have seen laevo-tartaric acid appear. Here again we have a case of simple asymmetry obtained from an inactive body; but in order to reach this result, it has been necessary, you see, to cause the intervention of the actions of asymmetry, the asymmetry of the natural proximate principles which go to make up the grain of mould.

"These are precisely the methods made use of by M. Le Bel in extracting from his racemates the simple active products. He had recourse to the employment of an asymmetrical substance or of a mould or a microbe.

"Further, these experiments indicate the existence of a line of demarcation between the mineral kingdom and the organic kingdom, since to imitate what nature does, that is to prepare a right-handed or a left-handed body, we are obliged to make use of peculiar kinds of action, of the action of asymmetry. The line of demarcation of which we speak is not a question of pure chemistry, of obtaining such and such products, it is a question of forces; life is governed by asymmetrical actions." . . . In a note M. Pasteur adds these words: "I am convinced that the double racemate of sodium and ammonium would not of itself under ordinary circumstances break up during crystallisation unless an asymmetric force were present, and if this is not an action of light or magnetism, I can readily believe that the force is due to some asymmetrical organic dust on the surface of the vessel in which the crystallisation takes place. Nothing would be simpler than to crystallise a solution of sodium-ammonium racemate with perfect exclusion of all organic dust. Under such circumstances the unchanged racemate should be obtained."

Discussion.

M. Wyrouboff said that the theories put forward by M. Pasteur with so much conviction and talent, in his lecture, appeared to him

to be opposed to all that is known to us regarding the properties of crystallised bodies. The theories are based upon a fundamental hypothesis, according to which natural (chemical) phenomena are subject to two kinds of action: symmetrical and asymmetrical; the former governing in the mineral kingdom and in the syntheses effected in our laboratories, the latter pertaining to the life process.

Asymmetrical bodies may be arranged, as is known, in two well characterised classes. Those of the first class, like quartz, sodium chlorate, benzil, cinnabar, are asymmetrical either in their internal structure and their external form, or only in their internal structure, no hemihedral face accompanying the rotatory power. All these bodies can be prepared artificially by starting with the elements; hence we must admit, looking at the matter from M. Pasteur's standpoint, that in our laboratories we have at our disposal at least some of the asymmetrical actions which he attributes exclusively to life; for, how shall we explain, by the aid of symmetrical actions alone, the existence of plagihedral faces of crystals and their relation to the rotatory power?

"The second category includes those bodies which are not asymmetrical in their internal structure, but have asymmetrical external forms and integrant molecules, or only the latter, for, between the rotatory power of the solution and the hemihedrism of the crystals, there is not that simple and necessary relation which was supposed to exist when only a few facts were known. These bodies have the rotatory power only in solution, and retain the power in all the compounds into which they enter. They are asymmetrical neither more nor less than the bodies of the first category; they are asymmetrical in a different sense.

"The bodies which have molecular asymmetry are the ones which M. Pasteur had in view when he asserted that they cannot be prepared synthetically.

"It should be remarked in the first place, that, among the great number of compounds which chemists have prepared synthetically, only very few have been studied crystallographically and examined with the polariscope. In the second place, the assertion is contradicted by the facts: racemic acid has been prepared synthetically, and it has been split up into dextro-rotatory and laevo-rotatory tartaric acids. To this proof, so clear and definite, M. Pasteur replies by suggesting a new hypothesis. He asserts that we really have to deal with some action of the asymmetrical order, some spiral movement, some magnetic influence, some organic dust, and he adds: 'Nothing would be simpler than to crystallise a solution of sodium-ammonium racemate with perfect exclusion of all organic dust. Under such circumstances the unchanged racemate should be obtained.' But what is the object of trying this experiment, when we consider that twenty years ago the racemate of the formula $C_4H_4Na(NH_4)O_6 + H_2O$ was prepared by M. Scacchi, who, in an admirable memoir, gave the exact conditions of its formation? He showed that the splitting of the acid was occasioned

only by the fact that the double ammonium sodium salts of the two tartaric acids are less soluble than the mixture of the two; that in elevating the temperature, the solubility of the dextro-acid increases more rapidly than that of the laevo-acid, and that there is a limit beyond which the mixture, becoming less soluble, the racemate alone is deposited. The phenomenon is so perfect that we can get at will from the same solution, properly concentrated and containing an excess of ammonium carbonate, either the racemate, or ammoniacal Seignette salt, or crystals of both at the same time. It is only necessary to vary the temperature between 17° and 26° . The racemate of sodium and potassium conducts itself differently: at 26° it always splits up; below this temperature it deposits sodium racemate, then Seignette salt, finally sodium racemate, each one of the deposits corresponding to the solubility of the salt, as M. Scacchi has shown.

"With sodium-thallium racemate the case is still different. M. Wyruboff has recently prepared this salt, and will soon describe its form. Seignette salt containing thallium crystallises, as is known, between 20° and 25° in voluminous soluble crystals in about half their weight of water. Neutral thallium racemate requires at these temperatures about nine parts of water to dissolve it; neutral sodium racemate about 2.5 parts.

"According to M. Pasteur, it would be impossible to say beforehand whether or not the racemate will be split into the dextro- and laevo-tartrates, the splitting being a result of mysterious forces acting asymmetrically.

"Nothing is easier, however, than to foresee the course of the phenomenon, if it really depends upon the greater or less solubility of the compounds taking part in the crystallisation. On evaporating at 25° we ought not to get the double tartrate; nor even the double racemate, unless it is—what it is not—less soluble than the neutral tartrate of thallium; we could get only thallium racemate; later, after the liquid is further concentrated, a little of the double racemate, and lastly, sodium racemate. This indeed is what is always observed. And it is so clearly a matter of solubility, that we may get the double racemate of sodium and thallium by two methods, apparently different, but based upon the same principle: we can crystallise the mixture at an elevated temperature, 40° for instance, or at the ordinary temperature, adding an excess of sodium racemate.

"Finally, we have the double racemate of sodium and rubidium, which under the proper conditions always breaks up at ordinary temperatures, and the two simple salts separate at higher temperatures.

"These examples enable us to solve without difficulty the general question as to the causes of the splitting of the racemates, which appears so complex and so mysterious to M. Pasteur, and which is nevertheless so simple. Why do not all the numerous racemates, simple as well as double, known up to the present time,

yield tartrates? Why is this action confined to the double salts of sodium, with potassium, ammonium and rubidium? Because, in these cases alone, one of the tartrates taken separately is less soluble at the ordinary temperature than the mixture of the two.

"We may hence state these rules, to which up to the present there are no exceptions known:

1. *Every racemate having a solubility less than that of the corresponding tartrate splits up;*

2. *Every racemate which is more soluble than the corresponding tartrate does not split up.*

Finally, concerning the case of double racemates,—and this applies to double salts of all possible acids:

3. *When two simple racemates, which are allowed to crystallise together, have very different solubilities, they are deposited separately. To get the double salt, the proportion of the more soluble salt must be increased.*

"The solubility being a function of the temperature, it is clear that these rules are valid for any given compound only at a definite temperature."

A propos of the communication of M. Wyruboff, M. Jungfleisch cited a number of facts which have led him to the opinion that the separation or non-separation of inactive bodies into their constituents is a result of the relations which exist between the solubilities. Thus, in a solution of sodium ammonium racemate, the dextro-tartrate resulting from the splitting up shows itself to be less soluble than the laevo-tartrate. Some experiments have indicated that differences of the same kind exist between the two active tartrates of sodium and potassium. Besides, it is known that the corresponding racemate obtained by M. Delffs was deposited in the neighborhood of 0° . Further, we may recall the tartrates of cinchonine of M. Pasteur: the marked differences which exist between their solubilities suffice to explain their separation. Finally, the phenomena observed by M. Jungfleisch on para-camphoric acid furnishes new insight from this point of view: during the cooling of a warm solution of this body between 80° and 40° , principally the laevo-acid is deposited, while the dextro-acid predominates in the crystals formed below 40° ; the solubility curves are so different that the two optically active acids can be separated by fractional crystallisation. If the mother-liquor is allowed to stand in the cold, para-camphoric acid is again formed.

M. Pasteur's Reply to M. Wyruboff.

"I am very much surprised that M. Wyruboff should have confused molecular asymmetry and the asymmetry in the arrangement in a crystal. Is not the difference between the two kinds of asymmetry demonstrated by the fact that fused quartz dissolved, sodium chlorate dissolved, strontium formate dissolved, have no action on polarised light; that, on the other hand, an asymmetrical

crystal, right or left handed, of one of these substances, as sodium chlorate for example, gives, when crystallised, two sorts of hemihedral crystals?

"M. Wyruboff objects to the hypothesis which I suggested in a note concerning my communication to the Chemical Society on the 22d of December, which was to the effect that the splitting of sodium ammonium racemate may be caused by organisms in the solution or on the crystallising dishes. As far as I am concerned, that is merely a preconceived notion, but I give it for what it is worth. *A priori* ideas, hypotheses, with all due deference to my opponent, are essential to scientific progress.

"If the experiment which I have referred to should not prevent the splitting of the racemate, I shall try whether the splitting may not be due to some other cause equally asymmetric, for example, light, or terrestrial magnetism.

"M. Wyruboff seems to think the matter is settled when he assures us that the conditions of the formation of the racemate and of the splitting of the racemate are now well known, and that they depend upon the greater or less solubility of the salts. But M. Wyruboff, in my opinion, seems not to comprehend the fact that the formation of the racemate is only perfectly natural, as all the racemates, with one exception, occur only as such; what is exceptional is that one racemate should split up. I cannot consider the opinion reasonable that finds the cause of the splitting in an influence of solubility. Why does the racemate of sodium and ammonium deposit crystals of two kinds, why does it give rise to the formation of complementary tetrahedrons? Why do these two tetrahedrons exist, and why not the octahedron which corresponds to them, which octahedron would have the solubility of the tetrahedral crystals? These facts, according to my idea, require explanation. I shall continue to believe, as long as I am not shown to be wrong, that the splitting can take place under the influence of asymmetry.

"M. Wyruboff, in another part of his remarks, calls my attention to the existence of bodies which are active towards polarised light, but which nevertheless have no asymmetry of form. He who reproaches me for not understanding the subject, appears not to be aware that I have formerly examined into this fact with much care, and that I have shown that it is easy, by means of artifices in crystallisation, to cause the appearance of asymmetric faces whenever internal molecular asymmetry exists. I cited the case of tartramide, the crystals of which formed in pure water never have hemihedral faces, but which show these faces when they are deposited from an ammoniacal solution. I cited the case of ammonium bimalate, which in crystallising from pure water never has hemihedral faces, and which has them when the liquid in which the salt crystallises is changed by a very simple process to which I refer.

"M. Wyruboff makes a great deal out of the following fact:

On adding ammonium citrate to ammonium (dextro) tartrate, the hemihedral faces appear on the other side of the crystal, and inversely for the laevo-tartrate, and, he adds, the hemihedrism may be made to disappear entirely. But this is only one of the accidents of crystallisation of which I have given many examples; I have proved that crystals of right-handed Seignette salt are sometimes met with which have left-handed hemihedral faces. A crystal may have a number of secondary forms. The hemihedral faces make a part of the secondary forms, and these show themselves or are absent according to the conditions of temperature, of the medium, etc., etc. One can not see why the external conditions of crystallisation should not overcome the influence of the asymmetric agency upon the internal structure of the molecules."

Experiments of M. Jungfleisch.

M. Jungfleisch describes some new experiments which tend to show that the dextro- and laevo-tartrates of sodium and ammonium have different solubilities in a solution of a mixture of the two salts. He introduced into a supersaturated solution of the racemate a right-handed crystal and a left-handed crystal. The two salts were deposited at once. The crystals were weighed in a number of cases and constant results were obtained. The following examples will indicate the character of these results:

I. Experiment with 1545 grams racemic acid:

Crystals of the first deposits: left, 557 gr.; right, 585 gr.

Crystals of the last deposits: left, 581 gr.; right, 569 gr.

II. Experiment with 1500 grams racemic acid:

Crystals of the first deposits: left, 561 gr.; right, 577 gr.

Crystals of the last deposits: left, 533 gr.; right, 488 gr.

In another case, starting with two kilograms of racemic acid, successive deposits were obtained as follows:

First crystallisation: laevo salt, 375 gr.; dextro salt, 400 gr.

Second crystallisation: laevo salt, 160 gr.; dextro salt, 181 gr.

Third crystallisation: laevo salt, 165 gr.; dextro salt, 190 gr.

Fourth crystallisation: laevo salt, 115 gr.; dextro salt, 115 gr.

Fifth crystallisation: laevo salt, 185 gr.; dextro salt, 150 gr.

In all the experiments the right-handed salt is at first deposited in greater quantity than the left-handed; its solubility is hence less than that of the left-handed salt. Inversely, in the second phase of the crystallisation the left-handed salt appears more abundantly than the right-handed.

Further, when a solution of sodium ammonium racemate is concentrated to such an extent that, on cooling, it deposits about half of the mixture of the two tartrates which it can yield, it is found that the mother-liquor has a rotatory power to the left, slight to be sure, but quite sufficient to be easily observed. Hence the left-handed salt exists in the mother-liquor in larger quantity than the right-handed salt; it is more soluble than the latter.

M. Jungfleisch finally states that the discussion between himself and M. Pasteur is based on a misunderstanding. M. Pasteur wishes to make a simple active body without passing through a body inactive by compensation, that is decomposable into right and left-handed substances; he wishes not simply to make racemic acid, which is decomposable into the two active tartaric acids, but to make directly a single one of the two latter. M. Pasteur wishes to follow the method of nature, which produces the dextro-acid and not racemic acid. This seems to M. Jungfleisch to be an entirely distinct problem, and it has not been solved up to the present, though the preparation of an optically active substance by methods independent of the life process has been accomplished. He is willing to go further and say that the problem of imitating the processes of nature has been solved neither for optically active nor for optically inactive substances. "The time when M. Berthelot established the possibility, till then denied, of producing synthetically the natural proximate principles is still not far removed, and although the results obtained in this way are as important as they are numerous, the state of science does not yet enable chemists to copy the actual *processes* of nature. Though M. Berthelot, M. Würtz, MM. Gräbe and Liebermann, or M. Baeyer, have effected the syntheses of alcohol, of the oil of mustard, of neurine, of alizarin and of indigo, they have not been able to copy the natural methods of formation of these substances, the natural methods remain unknown; they have, nevertheless, been of the opinion that a great step was taken in pointing out *any method whatever* by which these bodies can be produced without the intervention of the plants and animals."

I. R.

THE UNION OF BODIES BY PRESSURE.

It has been known for some time that two pieces of ice, when pressed together, provided their temperature is near their fusing point, unite and form one homogeneous mass. Nor is this the only case of the kind known to us. Powdered sodium nitrate, perfectly dry and pure, when placed in a stoppered bottle and allowed to stand a long time, becomes a solid block. This block, it is true, can be broken very easily. But suppose the particles could by some means be brought more closely together, would it not follow that the union would be more perfect? And provided the particles could be brought within the range of molecular action, would not the result be the same as if there had been fusion of the mass? Gases are liquified by causing their molecules to come within the range of each other's action. From this it would seem naturally to follow that substances possessing an affinity for each other could be made to unite and form a *chemical compound* by the same process as that used in the liquefaction of gases.

Led by this kind of reasoning, W. Spring, in 1880, was induced to try the effect of pressure on a large number of bodies. He subjected various substances to great pressure, and announced the result of his experiments to the Royal Academy of Belgium.¹

The apparatus used in effecting the pressure consisted of a stout lever moving on a horizontal axis. At the end of this lever heavy weights could be placed, and close to the axis there was a piston moving airtight in a steel cylinder. By the use of various weights at the extremity of the lever a pressure of 10,000 atmospheres was easily produced.

Filings of the various metals were placed in the cylinder and a pressure applied, increasing gradually until the desired effect was produced. In this way blocks of lead, bismuth, tin, zinc, aluminum, copper, antimony and platinum were obtained, that seemed to be homogeneous throughout. They had the specific gravity of ordinary fused metals; could be filed, sawed and hammered, and had all the other properties of homogeneous metals. Under the microscope there was no evidence of granular structure. This result, however, was not produced by one application of the pressure. The block obtained after the first application, was filed and the filings subjected again to increased pressure, until no evidence of pores could be detected under the microscope. Lead united under a pressure of 2000 atmospheres, bismuth at 6000, zinc at 5000 and copper at 6000. In no case was the temperature allowed to rise above 130°. At this temperature it was found that zinc united a little more readily than at a lower one. In all cases the block obtained was identical in appearance with that obtained by fusion. The bismuth, when struck, broke with a crystalline fracture, and possessed in common with the blocks of the other metals a highly metallic lustre. The ease with which the metals united seemed to be inversely proportional to their hardness.

A very interesting fact, noted in connection with lead especially, was its "flowing." In relation to this Spring says:² "Under a pressure of 5000 atmospheres, lead no longer resists the piston of the apparatus. It seemed *as if a liquid* were in all the cracks of the apparatus, and the piston was pressed to the bottom of the cylinder. When the apparatus was opened, thin coatings of the lead were found everywhere, which had the appearance of those obtained by plating."

When prismatic or amorphous sulphur was subjected to a pressure of 5000-6000 atmospheres, at the temperature 13°, an opaque block of rhombic sulphur was obtained, which was harder than that obtained by fusion. Its specific gravity was 2.0156, while that of the prismatic variety is 1.96. Its fusing point was 115°, that of ordinary rhombic sulphur being from 111° to 114°, and that of plastic sulphur 120°.

¹ Bulletin de l'Académie de Belgique, 2 série, 45, 746; 49, 323. Ann. de Chim. et de Phys., 5 série, 22, 170.

² Bull. de l'Acad. Belg. 2 ser. 49, 323; Ann. de Chim. et de Phys. 5 ser. 22, 170.

Amorphous phosphorus gave evidence of transformation into the crystalline variety.

Precipitated zinc sulphide under 5000 atmospheres gave a very hard, compact mass, whose exterior had a gray metallic lustre; the interior on the contrary appeared to be composed of a mass of crystal fragments, perfectly transparent, and reminded one of blende. The sulphides of lead and arsenic were obtained with the properties of the natural minerals to a greater or less extent. Carbon in the form of graphite united under a pressure of 5500 atmospheres, whereas that obtained by heating sugar gave not the slightest indication of union, but appeared to possess "great elasticity."

Copper filings and coarsely pulverised sulphur mixed together and subjected to 5000 atmospheres pressure, *combined chemically*, and formed a black crystalline mass of cuprous sulphide (chalcocite). An excess of sulphur had been used, and this excess could be detected with the microscope, disseminated through the mass of cuprous sulphide formed.

A coarse mixture of mercuric chloride and copper filings was put under 5000 atmospheres. There was complete change between the copper and the mercury. The copper had formed cuprous chloride with all the chlorine, and in place of the particles of copper little drops of mercury could be seen.

Dry potassium iodide and dry mercuric chloride, which gave no reaction under ordinary pressure, formed a red block of iodide of mercury and potassium chloride, when subjected to 2000 atmospheres.

In every case (except one¹) tried with success, the product obtained had a smaller volume and a greater specific gravity than those of the substances used. Every attempt made to obtain a solid product of less specific gravity than the mean of the specific gravities of the substances used, failed. In general it appears that "the substance takes the condition corresponding to the volume to which the substances used are compressed."

In order to test further the correctness of this law, a mixture of bismuth, cadmium and tin, in proportions to form Wood's metal, was taken and subjected to 7500 atmospheres pressure at the ordinary temperature. A solid block was obtained. This was filed and resubjected to the same pressure. The alloy formed fused at 70°. Lead, bismuth and tin were taken in proportions to form Rose's metal. The resulting block melted in boiling water.²

Besides the substances mentioned, Spring claims to have succeeded in producing the sulphides³ and arsenides⁴ of many of the metals, and to have produced them with all the properties of the

¹ A mixture of sodium carbonate and arsenic pentoxide gave off carbon dioxide and formed sodium arsenate.

² *Berichte der deutschen chemischen Gesellschaft*, **15**, 595.

³ *Berichte der deutschen chemischen Gesellschaft*, **15**, 999, and *Bull. de l'Acad. de Belg.* 3 ser. **5**, 492.

⁴ *Berichte, etc.*, **15**, 324; *Bull. de l'Acad. de Belg.* **5**, 229.

naturally occurring substances, especially as regards their crystalline structure.

Within the past year the accuracy of Spring's observations has been called into question by Friedel and Jannetaz of the French Chemical Society.

These gentlemen considered the question of so much importance as to warrant further study, and a repetition of Spring's experiments. Friedel¹ states that on subjecting various bodies to 10,000 atmospheres pressure he failed in every case to get complete union. Jannetaz,² working with Messrs. Neel and Clermont, subjected antimony, bismuth, tin, zinc, copper and iron to pressure, and obtained solid blocks, apparently homogeneous. The bismuth seemed to be more crystalline than the others, but was in reality only schistose in its structure. Bismuth, lead and tin in proportions to form Newton's metal, exhibited no indications of union.

Lead chloride formed a solid crystalline block, which probably owed its crystalline structure to the fact that the powder used was crystalline.

In compressing mercurous iodide a little escaped, and a small quantity of mercuric iodide was formed.

Powdered sulphur was mixed with zinc, iron, copper and lead filings respectively, in proportions to form blende, chalcocite, ferrous sulphide and galena. Pressure was applied, and the blocks formed were examined very carefully. They presented the general appearance of the substances to which their compositions corresponded. They were translucent at the edges and appeared to be crystalline. It was very difficult, however, to decide whether they were really crystalline or not, as under the microscope the crystalline powder used in the production of the blocks would interfere with the determination of the crystalline properties of the product.

On examination of their conduct toward heat, it was found that in the solid block, heat was propagated less easily in the direction of the pressure than perpendicularly to it. This has been shown to be a property peculiar to all bodies possessing a schistose structure. Now it is known that pressure produces this kind of structure, and Jannetaz claims that this is what has taken place in all the cases mentioned above. When the powdered blocks were treated with carbon bisulphide, the sulphur was dissolved and the particles of metal were left. In all cases, however, small quantities of the sulphides were formed, as was determined by grinding the product obtained with acid potassium sulphate, when a slight evolution of hydrogen sulphide was noticed. This is claimed as probably due to the heat produced by the pressure, and takes place more readily along the walls of the cylinder than in the interior of the mass. An incident is mentioned in this connection which shows that perhaps the heat produced by these enormous pressures is much greater than is generally supposed.

¹ Bull. de la Société chimique de Paris, **39**, 626.

² *Ibid.* **40**, 51.

On subjecting a piece of bell-metal to a pressure of some seven or eight thousand atmospheres, the block burst and pieces flew past the operators and fell some distance off. On picking them up they were found to be covered with a coating similar to that found on meteorites. This may have been due, however, to the "flowing" noted in connection with Spring's experiments.

Up to the present time Spring has not replied to the statements of Friedel and Jannetaz, so that it is impossible to decide positively as to the value of his results. Before attempting to explain or make use of them, we must wait until he has had an opportunity of repeating his experiments under conditions that preclude any possibility of error either in his methods or in the interpretation of his results. If he succeeds in maintaining his present position, there will be offered to us a ready explanation of many geological phenomena, among them the crystallisation of minerals at considerable depths under the surface of the earth.

W. S. B.

SOME RECENT TEXT-BOOKS ON CHEMISTRY.

A text-book which passes through ten editions in sixteen years must have good qualities. This remark certainly is applicable to Attfield's Chemistry,¹ a book which is so well known that it is hardly necessary to do more than note the appearance of this new and improved edition. It seems, however, desirable to point out that feature of the book which, in all probability, has made it so popular. There can be little doubt that it is its thoroughly practical character, the expression being used in the best sense. The author understands what the student ought to learn, and is able to put himself in the student's place and to appreciate his state of mind. Instead, therefore, of serving up a lot of "fundamental principles" to begin with, he skillfully brings the student in contact with the most important substances, and shows him how to study the most important reactions for himself. Instead of restricting his laboratory work to such reactions as may happen to be important for analytical purposes—in other words, instead of emphasising precipitates and disregarding the things unseen, as is too commonly done, he gives excellent directions for the study of synthetical reactions. Thus, under the head of Potassium, the student is shown how in test-tubes to *make* caustic potash, potassium bicarbonate, potassium iodide, the manganates, etc. So also in connection with the other elements, the chief compounds are treated in a similar way. Many of the compounds are, to be sure, introduced prematurely, the reason for this being the fact that they

¹CHEMISTRY: General, Medical and Pharmaceutical, including the chemistry of the U. S. Pharmacopœia. A Manual of the general principles of the science, and their applications in Medicine and Pharmacy. By John Attfield, F. R. S. 10th Edition. 8vo, 728 pp. Philadelphia: Henry C. Lea's Son & Co., 1883.

are used in medicine. This interferes with rather than enhances the value of the book. Thus again, under Potassium, we have the acetate, citrate, tartrate and the acid tartrate treated. So too, under Lead, we find oleate of lead, etc. Such treatment can only tend to confuse the student.

The part of the book which treats of "Organic Chemistry" has an antique flavor. The writer cannot be familiar with the present state of the subject. We don't ask him to cover his pages with structural formulas, but we do ask him to give the student some slight advantage of the beautiful and simple system of classification which is the result of modern studies of the compounds of carbon. He has given us a remarkable jumble.

A second American edition of Würtz's Chemistry¹ has appeared, the first bearing the date 1879. The commanding position occupied by Professor Würtz among chemists is a guarantee that his book is a valuable one. We examine it mainly with the object of seeing how a master deals with the subject. We may feel sure that the method of presentation adopted is the result of deliberate thought, based upon most comprehensive knowledge and experience in teaching. And what is the result? Does the author begin with an elaborate explanation of bonds and valence and structure and radicals and substitution? By no means. These subjects are not touched until page 222 is reached, and then cautiously—not dogmatically. It must be remembered that the author is one of the most ardent champions of modern structural chemistry, that he has himself done a great deal towards the development of the views now so commonly held. Yet he clearly sees the relations of these views to the facts, and his method of teaching is well calculated to keep these relations clearly before the mind of the student. The general introduction of the book would be of benefit to science.

Here and there occurs a dogmatic statement without explanation, as for example on page 106: "It (hydroxyl) is a monatomic group, and sulphuric acid is formed by the saturation of the affinity of the diatomic radical sulphuryl by two monatomic groups hydroxyl, which replace the two atoms of chlorine of sulphuryl chloride." . . . "The sulphur in sulphuric acid is *hexatomic*." Further, on page 13, is found this paragraph: "The molecules of oxygen . . . are each formed of two atoms," etc. Of course, to one well advanced in the subject there is nothing startling in such statements, but, to the beginner with no preparation, how must they appear?

We venture to express the hope that in future editions the translator, whose work in the main is well done, will adopt the system

¹ ELEMENTS OF MODERN CHEMISTRY. By Adolphe Würtz. Second American edition, translated and edited, with the approbation of the author, from the Fifth French edition, by Wm. H. Greene, Professor of Chemistry in the Philadelphia High School. London and Philadelphia: J. B. Lippincott & Co. 1884. 8vo, 770 pp.

of nomenclature proposed by Professor Watts for the use of those who prepare the abstracts for the Journal of the (English) Chemical Society. The suffix "ol" which the translator uses in the names benzol, toluol, xylol, &c., might better be reserved for bodies of alcoholic character. The English names most commonly used are benzene, toluene, xylene, &c.

Professor Richter's book has acquired a deserved popularity in Germany, and we are glad to welcome the American edition¹ which has been prepared by Professor Smith. The two features of the book which call for special mention are the use of the periodic law, especially as developed by Mendelejeff, as the basis of classification, and the treatment of the thermo-chemical phenomena involved in the principal reactions. There is much to be said in favor of the method of classification adopted. It cannot be applied rigidly and the author has not attempted to. He begins with hydrogen, and then takes up successively the halogen group, the oxygen group, the nitrogen group and the carbon group. In the nitrogen group are included phosphorus, arsenic, antimony, vanadium, niobium and tantalum. Bismuth is not included because its "metallic character . . . considerably exceeds its metalloidal."

At the end of the chapter on each group there is given a brief statement in regard to the thermal relations. It is time that the student's attention should be directed towards the thermal phenomena, so that, though the subject may not be fully developed, he may at least know the general character of the results already obtained and their bearing upon the science. It certainly is true that we do not as yet know enough about these complicated phenomena to warrant our using them as the basis of a strict scientific treatment of chemistry, but that should not prevent our teaching some of the simpler facts of the subject. The author first refers to the fundamental law according to which, when substances are brought together, that reaction takes place which gives rise to the greatest evolution of heat (the principle of greatest work). Of course, if this law were strictly true and without exceptions, and if we knew the heat evolved in the formation of every compound, it would be possible always to predict what the result of bringing together any given elements or compounds must be. Unfortunately, the law appears at times to fail, and, notwithstanding the labors of Thomsen, Berthelot and others, our knowledge concerning the figures representing the heat of formation of a very large number of compounds is exceedingly imperfect or entirely wanting, so that we cannot as yet make general use of the principle of greatest work, though probably the time is approaching when this will be possible. It is to be hoped that teachers of chemistry

¹ A TEXT-BOOK OF INORGANIC CHEMISTRY. By Prof. Victor von Richter. Authorised translation of Third German edition, by Edgar F. Smith, Professor of Chemistry in Wittenberg College, Ohio. Philadelphia: P. Blakiston, Son & Co. 1883. 8vo, 424 pp.

may prepare their students for the change by impressing upon their minds the importance of thermo-chemical phenomena.

A more careful use of English would have improved the translator's work and made the book more valuable for students. Many of the sentences are obscure in consequence of literal translation. In some cases words are incorrectly rendered. On pages 142, 144, for example, the two first members of the marsh gas series of hydrocarbons are called *methyl* and *ethyl*, instead of *methane* and *ethane*. The names used apply to the radicals CH_3 and C_2H_5 respectively, as is well known.

Finally, we cannot pass over a book¹ by Edwin J. Houston, inasmuch as it illustrates a tendency which is highly objectionable in the teaching of chemistry. The author begins with a consideration of theories which cannot be comprehended until chemical facts have been studied. He has evidently endeavored to make a book which can be used in "recitations." The sentences are short and are intended to be learned by heart. They are for the most part correct enough, but, as a rule, they are not adapted to the use of the beginner. When a boy is about to begin the study of chemistry, it not only does no good, but it does positive harm, to make him learn a lot of definitions of words. Give him the things so far as possible; don't muddle his mind with words more than is absolutely necessary. One cannot avoid a feeling of indignation on reading in the introductory part of a book on elementary chemistry, such bald definitions as:

"Acids are substitution compounds formed by the combination of an electro-negative substance with hydroxyl."

"Bases are substitution compounds formed by the combination of an electro-positive substance with hydroxyl."

"Salts are substitution compounds in which an electro-positive radical or element is united to an electro-negative radical or element by means of oxygen."

These definitions are merely so many high-sounding words. They do not convey any sort of an idea to the mind concerning the nature of the substances defined. This kind of teaching is, we are happy to say, fast losing ground, but the appearance of this book arouses a fear that it still may be in more extensive use than we hoped.

It is unnecessary to go into details regarding the faults of the book. If any one should decide to use it, we earnestly advise the omission of all that pertains to chemical theories. The treatment of the facts is fairly good, but we cannot see that it is any better than that of a dozen other elementary text-books now in use.

I. R.

¹THE ELEMENTS OF CHEMISTRY. For the use of Schools, Academies and Colleges. By Edwin J. Houston, Professor of Physical Geography and Natural Philosophy in the Central High School; Author of "Elements of Physical Geography," "Elements of Natural Philosophy," etc., etc. Philadelphia: Eldredge & Brother. 1883. 8vo, 444 pp.

REPORT ON GLUCOSE, prepared by the National Academy of Sciences, in response to a request made by the Commissioner of Internal Revenue. Washington, Government Printing Office, 1884.

This report contains a great deal of information in regard to the manufacture of starch-sugar and the nature of the products obtained. There are twenty-nine factories in the United States, using, as nearly as can be estimated, 43,000 bushels of corn per day. The products are of various grades, which appear in commerce under the following names: (*a*) The liquid varieties: Glucose, mixing-glucose, mixing-sirup, corn-sirup, jelly-glucose, confectioners' crystal glucose. (*b*) The solid varieties: Solid grape-sugar, clipped grape-sugar, granulated grape-sugar, powdered grape-sugar, confectioners' grape-sugar, brewers' grape-sugar.

The most general purposes for which starch-sugar is used are: 1. For the manufacture of table-sirup; 2. A substitute for barley-malt in the brewing of ale or beer; 3. As a substitute for cane-sugar in confectionery; 4. For the adulteration of cane-sugar, to which it is added to the extent of 20, or more, per cent.; 5. For the manufacture of artificial honey; 6. For the manufacture of vinegar.

The transformation of the starch into dextrose is effected in most of the factories by means of sulphuric acid, though in some oxalic is used, and the use of phosphoric acid has been suggested. The normal products of the transformation by means of these acids are, as is well known, dextrose, maltose and dextrin. The commercial products consist of these substances in different proportions, the liquid products containing more dextrin and maltose than the solid products. In the latter the analyses showed the presence of from 72 to 73.4 per cent. of dextrose, and from 4.2 to 9.1 per cent. of dextrin. In the "glucoses" or liquid products analysed, the amount of dextrose was found to vary from 34.3 to 42.8 per cent., and the amount of dextrin from 29.8 to 45.3 per cent. The mineral constituents were found to be present only in insignificant quantities and to be of harmless nature.

In the fourth subdivision of the report the subject of the relation of starch-sugar to health is discussed. The question, "Is the use of 'glucose,' or 'grape-sugar,' injurious to health?" is asked, and the report then proceeds:

"This is certainly one of the most important questions that can be asked regarding the substance under consideration. It has been discussed very freely, but on a very insufficient basis of facts. Indeed, so far as the products made from corn-starch are concerned, it appears that no experiments have ever been made with reference to their effects upon the system. It is essential in a discussion of this subject to keep clearly in mind the fact, that while it is undoubtedly true that the pure chemical substances, dextrose, maltose, and dextrin, are not injurious, there may be other substances present in

small quantities in the commercial products, and that these are capable of producing injurious effects; or it may be true that when the commercial products are changed by fermentation, substances of injurious character are formed or left unfermented.

"In Germany, where large quantities of dextrose are made from potato-starch, experiments bearing upon the question of the presence of injurious constituents have been made with the commercial products. Some of the results obtained indicate that after fermentation of potato-sugar there are left substances which are injurious, while others indicate that this is not true. Among those who have experimented on the subject, A. Schmitz, Nessler, and Freiherr von Mering should be specially mentioned. Schmitz' fermented potato-sugar, and, evaporating the products down to small volumes, administered known quantities of the residues to cats and dogs, and in a few cases to human beings. The results obtained were uniform, and showed that the substance caused sickness, as headache, sweating, and loss of appetite.

"Later, Nessler² undertook similar experiments, and obtained similar results. He experimented upon his assistant and himself. One of his experiments is here described. He allowed a 20 per cent. solution of potato-sugar to ferment after the addition of a small quantity of hops. After the fermentation was over, the liquid was filtered, a litre evaporated down to a sirup, and then diluted up to 100 cc. This solution had a disagreeable, bitter taste. Nessler took 50 cc. of it at 7 A. M., and the same quantity at 10 A. M., each portion corresponding to 100 grams of potato-sugar. Toward noon he began to feel uncomfortable, but not so much so that he could positively attribute his condition to the beer extract. At 2 P. M., the residue from 100 grams potato-sugar was again taken; and now in about an hour there followed profuse perspiration and violent headache, both of which continued until night. A few days later, his assistant took the residue from 90 grams of sugar, the fermented liquor having been evaporated down to two-fifths its original volume. He soon experienced difficulty in breathing and broke out in a cold sweat; at dinner he had no appetite, and was obliged to throw up the little soup he did take. In the afternoon he had a violent headache, which continued until evening.

"Nessler concludes his paper with these words: 'It is hence beyond a doubt true that in the liquid obtained in the fermentation of potato-sugar there are substances injurious to health. If the question is asked whether this is true of all commercial potato-sugars, as well as of the sugar examined, we cannot give a definite answer.

"In the case of all varieties of potato-sugar thus far examined, there remains after evaporation of the fermented liquid a bitter-tasting extract, which turns the plane of polarisation to the right,

¹ Beiträge zur diätetischen Beurtheilung des gallisirten Weines. Bonn, 1878.

² Wochenblatt des landwirthschaftlichen Vereins im Grossherzogthum Baden, 1880.

and it is very probable that all of them may act injuriously upon the health, in varying degrees, according to the greater or less purity.

"'As in buying the sugars it is not possible to determine whether the harmful substances are present or not, potato-sugar should not be used for the preparation of beverages,'¹ until it can be prepared in perfectly pure form.'

"Directly opposed to the results of Schmitz and Nessler are those obtained by Freiherr von Mering.²

"This writer experimented upon dogs, cats, rabbits, and human beings, in much the same way as Schmitz and Nessler had done, and he concludes that the unfermentable residues from potato-sugar are not at all objectionable.

"Later, Schmitz³ replied to Von Mering, upholding his first results.

"It hence appears doubtful whether there are injurious substances in potato-sugar, and it is highly desirable that the experiments on this subject should be repeated by those who have not thus far taken active part in the discussion. Even though it should eventually be shown that potato-sugar is or is not objectionable, it would not necessarily follow that the same is also true of maize-sugar.

"As, so far as we know, no experiments had been made upon starch-sugar, we carefully repeated the experiments described above, using several of the samples of glucose and grape-sugar, the analyses of which are given in the preceding part of this report.

"We were fortunate in securing for this work the assistance of Dr. J. R. Duggan, of the Johns Hopkins University, who has for some time past been occupied in experiments upon fermentation, and who is hence fully familiar with all the precautions necessary to secure reliable results. The fermentations were carried on in a new cellar, which fortunately chanced to be available, so that the danger of abnormal fermentation was reduced to a minimum.

"Pure glucose cannot be fermented by the simple addition of yeast in small quantity; for yeast, like all living matter, requires certain nitrogenous and inorganic materials for its own nourishment. As has been shown by Pasteur, this want may be supplied by the addition of certain salts, such as ammonium tartrate, calcium phosphate, &c.; but as these cannot be added in exactly the necessary proportions, some would be likely to remain in the solution after fermentation was complete, and, if taken into the stomach along with the glucose residue, would probably produce an effect of its own which might be attributed to the glucose.

"It is not easy to obtain in sufficient quantity a liquid furnishing a proper medium for the growth of yeast which does not also contain glucose; and, for this reason, it was first necessary to deter-

¹ One of the uses to which potato-sugar is put in Germany is as an addition to poor wine.

² Deutsche Vierteljahrschrift für öffentliche Gesundheitspflege, 14, 325.

³ *Ibid.* 431.

mine the effect, if any, of the unfermentable residue from this glucose.

"Experiments Nos. 1, 2, and 3 were made for this purpose. The nutrient liquid used was barley-wort, on account of the fact that it is most commonly used in brewing for commercial purposes.

"This liquid contains much more nitrogenous matter than is necessary to support the yeast during its fermentation, and therefore it still forms a good medium for the growth and development of yeast after it is considerably diluted with a solution of glucose.

"The method of experimenting was as follows: The barley-wort, of the concentration usually employed for making beer, was mixed with the glucose solution, and the whole heated to boiling by passing steam through a coil of black-tin tubing placed in the tub. The tube was then connected with the hydrant, and water passed through it until the solution was well cooled. It was then allowed to flow slowly over a wide board, for the purpose of thoroughly aerating it. The temperature was reduced to about 10° C., and about a pint of yeast added. Fermentation was carried on in a cool vault, and was allowed to continue until very little sugar was left in the solution and the yeast had all settled to the bottom of the tubs. A sufficient quantity of beer was then siphoned off and evaporated slowly over the water-bath to about one-tenth its volume. The residue consisted principally of dextrin, nitrogenous matter from the wort, glycerin, succinic acid, and probably other products of fermentation in very small quantities. It formed a thick, dark-colored sirup, of very disagreeable taste, especially when wort containing hops had been used. For this reason, sweet-wort was used in most of the experiments. All of the fermentations were carried on by the low process—that is, with bottom yeast at a temperature of from 8° to 10° C.

"Two experiments were tried with the high process, but it was found to be impracticable on the small scale, on account of the development of bacteria, due to the higher temperature. As the difference in the two processes is essentially one of temperature only, there is no reason to suppose that they could in any way give different results.

"The amount of yeast added to each tub was about one-half litre. This was carefully examined with the microscope, both before and after fermentation, to guard against the presence of foreign ferments that might produce injurious products. The glucoses used were of the various manufactures already mentioned, and embraced the different grades of solid and liquid products.

"The extracts were taken at different hours of the day, both before and after meals. The quantity usually taken contained the residue from 125 grams of glucose; but in experiment No. 8 this quantity was increased so as to correspond to 200 grams. It seems useless to try still larger quantities, for it is probable that if much more was taken the normal products of fermentation, such as succinic acid, would produce some effect.

"*Experiments 1 and 2.*—Thirty litres of sweet-wort and the same quantity of hopped wort were separately fermented, the process lasting, in each case, one week. Five litres of the resulting liquid were evaporated to 750 cc., and 300 cc. of the extract taken internally. The same experiment was tried by two individuals, but no effect was produced. The amount of extract taken corresponded to two litres of the beer.

"*Experiment 3.*—In this experiment there were used 15 litres of sweet-wort, to which were added 15 litres of a 12.5 per cent. solution of cane-sugar. Five litres of the liquid were evaporated to 500 cc., and 200 cc. of the extract taken, with no effect. The amount of extract taken represented 125 grams of cane-sugar.

"*Experiment 4.*—Fermented 15 litres sweet-wort and 15 litres of a 12.5 per cent. solution of grape-sugar. (Sample No. 12.) Five litres of the liquid were evaporated to 500 cc., and 200 cc. taken. No effect was produced. On the following day, the same amount of residue was taken, and with no effect. The amount of extract taken corresponded to 125 grams of glucose in each experiment.

"*Experiment 5.*—Fifteen litres of sweet-wort and 15 litres of a 12.5 per cent. solution of grape-sugar (Sample No. 7) were fermented. The same amount of extract was taken as in the last experiment, with the same results.

"*Experiment 6.*—The details of this experiment were exactly the same as those of the last. The substance was a commercial glucose. (Sample No. 14.)

"*Experiment 7.*—Fifteen litres of hopped wort, with 7.5 litres of a 25 per cent. solution of commercial glucose (Sample No. 1), were fermented. Four litres of the fermented liquid were evaporated down to 400 cc., and of the residue 150 cc. were taken. No effect was felt.

"*Experiment 8.*—Fifteen litres of hopped wort and 7.5 litres of a 25 per cent. solution of grape-sugar (Sample No. 13) were fermented. Five litres of the fermented liquid were evaporated to 500 cc., and 200 cc. taken. No effect was felt. The extract represented 160 grams of grape-sugar.

"The experiments described above occupied about two months, during which time Doctor Duggan repeatedly took large quantities of the extracts. At the end of the experiments, and during the entire period, his health continued excellent.

"There was nothing whatever to indicate that the extracts contained anything injurious to health, and the conclusion seems to be fully justified that the samples examined by us, and which we have every reason to believe were fair average samples of the substances found in the market, contained nothing objectionable from a sanitary standpoint. In the experiments the experimenter took into his system everything that could possibly be objectionable contained in from 120 grams to 160 grams of the glucose, or

grape-sugar, *i. e.*, from a quarter to a third of a pound. It must be borne in mind, further, that the extract which was taken into the stomach must have contained any objectionable mineral as well as organic substances present in the glucose employed. Hence, the results seem to be final as regards the injurious nature of glucose, or grape-sugar, made from maize.

"These experiments extended over a period of only about two months. On the question, therefore, whether any injurious effect would follow the continuous use of this material, the committee has no information.

"Our experiments have, of course, no direct connection with those of Schmitz, Nessler, and Von Mering, already referred to. These gentlemen experimented upon potato-sugar as furnished by manufacturers in Germany. Our conclusions are valid only for maize-sugar as furnished by manufacturers in this country.

"It should be further remarked that, although our experiments show conclusively that the products of fermentation of glucose are not dangerous to health, it does not necessarily follow that beer made by the fermentation of glucose is as good as that made in the usual way. That is a matter which does not fall within the scope of our investigation."

The report was prepared by a committee of the National Academy of Sciences, which consisted of Professors George F. Barker, of the University of Pennsylvania; W. H. Brewer, of Yale College; Wolcott Gibbs, of Harvard College; Charles F. Chandler, of Columbia College; and Ira Remsen, of Johns Hopkins University.

ON THE DISCOVERY OF THE PERIODIC LAW, AND ON RELATIONS AMONG THE ATOMIC WEIGHTS. By JOHN A. R. NEWLANDS, F. I. C., F. C. S., etc. London: E. & F. N. Spon. 8vo, 39 pp.

This book has been published in order to place before chemists the proof that the author was the first one to point out the existence of the periodic law relating to the properties of the elements as functions of their atomic weights. In the preface the author says: "This little book contains an exact reprint of all the papers on Relations among the Atomic Weights, and on the Periodic Law (provisionally termed the 'Law of Octaves'), written by myself, and printed in the *Chemical News*, some years before M. Mendelejeff had published anything on the subject of the Periodic Law. . . .

"Having been the first to publish the existence of the periodic law more than nineteen years ago, I feel, under existing circumstances, compelled to assert my priority in this matter.

"That both Mendelejeff and Lothar Meyer have done a good deal to develop the periodic law is admitted, but this admission by no means assumes that either of these eminent chemists was the

first discoverer of the law in question. As a matter of simple justice, and in the interest of all true workers in science, both theoretical and practical, it is right that the originator of any proposal or discovery should have the credit of his labor. . . .

"To sum up: I claim to have been the first to publish a list of the elements in the order of their atomic weights, and also the first to describe the periodic law, showing the existence of a simple relation between them when so arranged."

A careful examination of the republished papers shows that the author really had a fairly clear notion of the periodic law as far back as 1864, while, as is well known, the papers of Mendelejeff and Lothar Meyer appeared in 1870.

The state of the case appears to be about as follows: Several chemists prior to 1864 had pointed out simple relations between the atomic weights of certain groups of similar elements, as sulphur, selenium and tellurium; chlorine, bromine and iodine, etc., etc. Then Newlands arranged all the elements in one table, mainly with the object of showing numerical relations between the atomic weights. In a communication to the *Chemical News*, dated August 18, 1865, Mr. Newlands said: "If the elements are arranged in the order of their equivalents, with a few slight transpositions, as in the accompanying table, it will be observed that elements belonging to the same group usually appear on the same horizontal line." In the table referred to the symbols H, F, Cl, Co and Ni, Br, Pd, I, Pt and Ir, form the first horizontal line. While, thus, fluorine, chlorine, bromine and iodine appear in the same line, cobalt and nickel, palladium, platinum and iridium are also found in this line, a fact which would lead one to suspend judgment in regard to the value of the proposed table. Mr. Newlands in the same paper says: "It will also be seen that the numbers of analogous elements generally differ by 7, or by some multiple of 7; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music." The numbers here mentioned are those designating the position of the elements in the table. Thus, hydrogen is 1, lithium 2, glucinum 3, boron 4, &c., and the above statement is the first one bearing upon the fundamental principle involved in Mendelejeff's and Lothar Meyer's tables, viz. that the elements naturally fall into groups of seven, each eighth having properties similar to those of the first in the series. For this discovery Mr. Newlands should certainly receive credit. It is, however, doubtful whether, without much greater development, the periodic law would have received the serious attention of chemists. While the arrangement in groups of seven is made use of by M. Mendelejeff, that really forms only the simplest part of his system. The fact first pointed out by Mendelejeff that two such short series of seven elements, together with a sub-series of three others, combine to form a long period, alone makes it possible to arrange all the elements in one table in such a way as to bring allied elements

together. When this fact was discovered what wonderful results followed! When the relations which exist between the atomic weights and the properties of the elements were so clearly pointed out by M. Mendelejeff, chemists no longer doubted. They saw at once that a law of fundamental importance had been discovered. As regards the question whether the law in its perfected form was first discovered by M. Mendelejeff or by Lothar Meyer, it seems to be true that these chemists were working on the subject in much the same way at the same time, but that, as a matter of fact, Mendelejeff's paper was published, or at least read publicly, a few months before Meyer's appeared. The names of both these gentlemen will certainly always be remembered in connection with the periodic law, and that of Mr. Newlands cannot well be forgotten.

I. R.

NOTES.

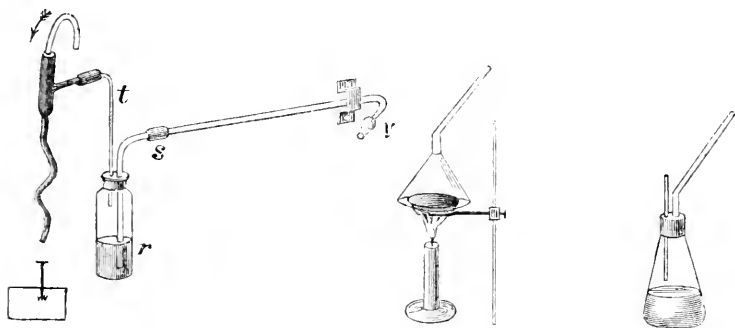
To remove Noxious Vapors in the Evaporation of Corrosive Liquids.

In the chemical laboratory of Vassar College, a Richards aspirator with the necessary water supply and waste pipes is furnished to every student. It is used not only for rapid filtration, but in other processes wherever a current of air is needed. I have also applied it to the process of evaporation, first, for the purpose of carrying away the noxious vapors arising from corrosive liquids, and second, for evaporation in partial vacuo.

To fit the aspirator for general use it is mounted upon one corner of the student's work-table in the manner shown in Fig. 1. A small glass tube *t*, joined to the exhaust pipe by rubber tubing, passes through the air-tight cork of an eight-ounce wide-mouth bottle. A larger tube reaches nearly to the bottom of this bottle. The tube *sv* is a little smaller and enters the end of this larger tube, while a piece of rubber tubing stretched over the junction makes a tight but flexible joint. The outer end at *v* has a rubber tube stretched over it, by means of which connection is made with whatever apparatus is to be exhausted. Disconnection is made at this point *while the aspirator is still running*, to prevent the water from the bottle *r* backing over into the vacuum which has been produced in the filter bottle or other vessel employed.

The Ventilating Funnel.—The stem, six or eight inches long, of a glass funnel is bent at a right angle near the body. The end of the stem is thrust through the rubber tubing, and into the some-

what larger tube *v*. The evaporating dish is then brought up under the mouth of the funnel until the funnel rests upon it (Fig. 2). The aspirator is then started and the heat applied. The current of air flowing over the edge of the evaporating dish into the funnel



carries the fumes with it to be condensed in the reservoir bottle *r*, or off with the stream of water into the sink. The edge of the funnel may rest *inside* the evaporating dish with the same result; the same funnel is thus used with dishes of varying diameter. Two sizes are at present in use; one of 3 inches diameter for evaporating dishes, another of $1\frac{1}{2}$ inches for crucibles. The evaporation of acids to dryness is conducted on the open tables without annoyance from their fumes, by means of this simple artifice.

The Flask.—Let the cork of a flask be pierced with two holes, one for a bent tube to enter the aspirator tube *v*, the other for a straight tube which may be adjusted so that its lower end will be little above the liquid within. A current of air will then pass through this straight tube, over the surface of the corrosive liquid in the flask and sweep its fumes away into the waste.

To evaporate in partial vacuo, provide the flask with a cork carrying the bent tube only. No air can enter, and the aspirator will then create a vacuum, to a degree depending on the head of water at command.

LE R. C. COOLEY.

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F. W. C.

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Contributions from the Sheffield Laboratory of Yale College.

XVIII.—THE SEPARATION OF ZINC AND NICKEL.

BY THOMAS B. OSBORNE.

Having experienced considerable difficulty in separating zinc and nickel according to the directions given in Fresenius' Quantitative Analysis, I determined to find out the exact conditions under which the best separation could be effected. I prepared several solutions of zinc and nickel sulphates, containing about .4 gram zinc and .3 gram nickel, in 300 cc. of water slightly acidified with sulphuric acid. To these I added carbonate of soda until a slight but permanent precipitate was formed, which remained after stirring and standing, and then added four drops of hydrochloric acid (sp. gr. 1.1) to the first, six to the second, eight to the third, and so on, adding eighteen to the last. Into these liquids I led sulphuretted hydrogen gas for an hour and a half, and during the precipitation added a solution containing enough sodium acetate to react with half the acid set free by the precipitation of the zinc. On standing, all the zinc and nickel precipitated from the solution containing four drops of acid, and pure white zinc sulphide was only obtained in those solutions containing ten or more drops, and the filtrate from these contained no zinc.

I then sought to determine how much hydrochloric acid the solution might contain without keeping the zinc in solution. On increasing the amount to 2 cc. hydrochloric acid (sp. gr. 1.1) in

300 cc. of water, I found that a very little zinc remained in solution after passing the sulphuretted hydrogen gas two hours. The rule I established from the above experiments was to add carbonate of soda solution until a slight but permanent precipitate formed, then 1 cc. hydrochloric acid (sp. gr. 1.1), and gradually during the precipitation of the zinc 50 cc. of a solution containing enough sodium acetate to react as near as may be with one-half the acid set free. Sulphuretted hydrogen gas was passed an hour and a half. In this way a certain separation can be secured, and the zinc will be snow white.

Brunner's directions, if accurately followed, will give a good separation, but they are rather indefinite on the vital point, namely, the amount of hydrochloric acid to be added. He says a *few* drops should be added, which if taken to mean ten or twelve would give good results if too much zinc were not present; for if a large amount of zinc were in solution, its precipitation would set free so much acid that "the few drops of a very dilute solution of sodium acetate" which he adds, would not suffice to effect its complete precipitation. His theory of the action of sodium acetate made the amount of this quite independent of the amount of zinc, as he considered it as forming zinc acetate, which was precipitated by hydrogen sulphide, and the acetic acid thus set free reacted with more zinc until all was precipitated. The office of sodium acetate is of course to form acetic acid and sodium chloride or sulphate as the case may be, reacting with the acid set free by the precipitation of the zinc. Fresenius is more explicit in regard to the amount of hydrochloric acid which should be added, but he recommends only two or three drops, which in most cases is too little. The basic zinc carbonate is quite soluble in a solution of carbonic acid, and consequently a *permanent* precipitate is often not obtained until there is an appreciable excess of sodium carbonate, which will sometimes require as much as three or four drops of hydrochloric acid to neutralise it. Hence to be certain of a good separation, at least 1 cc. hydrochloric acid (sp. gr. 1.1) should be added; and that the amount of free hydrochloric acid shall remain as nearly constant as possible, enough sodium acetate should be added to react with about one-half the acid set free by precipitation. It is hardly safe to add more, lest some nickel may be thrown down. When ammonium salts will not interfere with the subsequent determination of the nickel, ammonia is much more convenient to use than sodium carbonate. This should be added until a precipitate is

formed, then hydrochloric acid until this precipitate is just dissolved, and two or three drops added in excess, the hydrogen sulphide passed and the sodium acetate solution added as before. If ammonia gives no precipitate, owing to the presence of too much ammonium salts, a neutral reaction with test paper may be obtained, and an excess of four or five drops of hydrochloric acid added. Ammonia is much more easily employed than carbonate of soda, and when the nickel is determined by precipitation with ammonium sulphide, and then as metal with the battery, the ammonium salts are beneficial rather than otherwise.

XIX.—THE SEPARATION OF ZINC IN ORES, &c.

BY THOMAS B. OSBORNE.

Although Brunner¹ states that zinc cannot be separated from iron by his method for the separation of zinc from nickel, I have found that, under certain conditions at least, it can be done, and that, too, very perfectly. I tested for iron several precipitates of zinc sulphide precipitated from solutions containing iron, and obtained only the very faintest tinge of red with ammonium sulphocyanate. The filtrates from these sulphides I examined with care for zinc and found none; I then tried this process for the separation of zinc from its ores and obtained very accurate results.

Silica was first removed from the ores, and then any iron that was present in the ferric state reduced by warming with sulphurous acid, so that there might be as little hydrochloric acid as possible liberated from the reduction of iron by the subsequent passage of hydrogen sulphide.

The solution was cooled and ammonia added till a slight permanent precipitate formed. This was dissolved in hydrochloric acid (sp. gr. 1.1), and four or five drops added in excess. The volume was then brought to 300 cc. and hydrogen sulphide passed one hour and a half. Fifty cubic centimeters of a solution containing a sufficient quantity of sodium acetate to react as nearly as could be estimated with one-half the acid set free by the precipitation of the zinc, were added gradually. The zinc sulphide was filtered, washed, dissolved in hydrochloric acid, and precipitated with sodium carbonate and weighed as oxide.

¹ Dinger's Polyt. Jour. 150, 369.

When a large amount of zinc is precipitated in this way, sodium acetate should be added in such quantity that there will be only about .2 gram of hydrochloric acid gas left free in 300 cc. of the solution after precipitating all the zinc. As it is not always possible to know approximately how much zinc is present, the proper amount of sodium acetate to add cannot be determined with accuracy. But some latitude is permissible here, as the zinc can be precipitated in a solution containing even .4 gram hydrochloric acid gas in 350 cc. of water, as shown by Eliot and Storer's¹ experiments and confirmed by my own. It should be borne in mind, however, that the more acid there is present the greater is the liability of an incomplete precipitation.

Several analyses by this process gave results agreeing closely with analyses made by Dr. A. B. Howe of this laboratory, who removed iron by precipitating it twice as basic ferric acetate, and separated zinc from manganese as sulphide in an acetic acid solution, determining zinc finally as oxide. The results of these analyses were as follows:

By direct precipitation as sulphide in hydrochloric acid solution,

ZnO	Ores.			Slag.
	27.73	20.11	27.78	
				2.08

By separating iron as basic acetate, &c.

ZnO	27.87	20.10	27.23	2.04
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Zinc was determined by this method in three solutions made up as follows:

Ca(OH) ₂	.3	gram.	.2	gram.	
MnCl ₂	.2	"	.2	"	
Al ₂ (SO ₄) ₃	.2	"			
MgSO ₄	.2	"	.2	"	
FeSO ₄	.5	"	.5	"	4.6
Zinc	.3392	"	.3040	"	.0202
Zinc found,	.3410	"	.3035	"	.0210

I found that sulphuric acid (1 volume strong acid to three of water) can be used as well as hydrochloric acid (sp. gr. 1.1) to keep the iron and other members of the first four groups (according to Fresenius) from precipitating with the zinc. It should be used in the same amount by volume. By this process zinc can be determined in an ore in five or six hours, as the zinc sulphide need not settle before filtering if the amount of free hydrochloric acid is small.

¹ Mem. Am. Acad. Arts and Sciences 8, 95.

THE QUANTITATIVE ESTIMATION OF CARBON IN ORDINARY PHOSPHORUS.

BY IRA REMSEN AND E. H. KEISER.

In our last communication¹ in which we furnished proof of the presence of carbon in ordinary phosphorus, we referred to some attempts made by us to estimate the carbon quantitatively. These attempts were not satisfactory. We have since continued the work, and have succeeded in devising a method which gives fair results. In brief it consists in oxidising a known weight of phosphorus by means of pure concentrated nitric acid, removing the oxides of nitrogen from the escaping gases, collecting and weighing the carbon dioxide. The apparatus used is, first, a glass-stoppered retort of about 500 cc. capacity. This is placed with the neck inclined upward at an angle of about 30°, and connected by means of glass tubing and gypsum joints with one of the wash bottles described in our last paper. This in turn is connected in a similar way with a combustion tube placed on a furnace. At the other end of the combustion tube connection is made with two wash bottles like the one above referred to. In the retort are placed two to three hundred cubic centimetres of pure nitric acid of specific gravity 1.2, and a weighed amount of ordinary phosphorus. In the first wash bottle there is pure water. The combustion tube is filled to about half its length with granulated metallic copper, and a short layer of granulated copper oxide. In the first of the last two wash bottles is pure water, and at the proper time a clear solution of baryta water containing some caustic soda is brought into the second. Finally this last wash bottle is protected from the air by a tube filled with caustic soda. After the apparatus is arranged as thus indicated, a slow current of air free from carbon dioxide is drawn slowly through it until all the original air is displaced. Now the retort is closed by means of a glass stopper, the baryta water and caustic soda are introduced into the last wash bottle, and the heating of the retort and the combustion tube is begun. A very small flame is used, and a regular, slow evolution of gas is secured. A portion of the tetroxide of nitrogen is, of course, decomposed by the water in the first wash bottle; what

¹ This Journal 5, 424.

remains passes on, together with the other oxides, to the heated copper which decomposes them. The copper oxide serves to oxidise any carbon monoxide which may possibly have escaped complete oxidation.

It will thus be seen that the gases do not come in contact with organic matter at any point. A blank experiment showed that, when purified air was passed through the heated nitric acid, and in other respects treated as in the experiments with phosphorus, no precipitate was formed in the baryta water. When the phosphorus was introduced into the nitric acid, however, a precipitate was clearly perceptible in about half an hour from the beginning of the heating. It increased and became very decided in the course of two or three hours, the time usually occupied by the experiment. When the oxidation is finished, air free from carbon dioxide is again slowly drawn through the apparatus until the gases have been displaced. The bottle containing the barium carbonate is then removed, closely stoppered, and the precipitate allowed to settle. It is then rapidly filtered off with the aid of a filter pump, washed, and dissolved in dilute hydrochloric acid. The effervescence caused by the acid leaves no room for doubt as to the character of the precipitate. The barium is now estimated as sulphate. The filtrate from the sulphate was carefully examined for compounds of phosphorus, but not a trace was found. In two cases the carbon dioxide was collected directly in caustic potash contained in bulbs which were weighed before and after the experiment. In three analyses a considerable quantity (from sixty to eighty grams) of phosphorus was placed in the retort, and the oxidation continued for about three hours. The unoxidised phosphorus was then weighed, the difference between this weight and the original weight of the phosphorus showing the amount oxidised. Closely agreeing results can hardly be expected, yet it will be seen that the agreement is fairly good, if we leave out the second analysis, which for some unknown reason gives a considerably larger percentage than the others. The results of six analyses are here given:

I. 6.2272 grams phosphorus gave 0.0300 gram $\text{BaSO}_4 = 0.0057$ gram $\text{CO}_2 = 0.0016$ gram $\text{C} = 0.026$ *per cent. carbon.*

II. 7.9545 grams phosphorus gave 0.0324 gram $\text{CO}_2 = 0.0088$ gram $\text{C} = 0.111$ *per cent. carbon.*

III. 8.8041 grams phosphorus gave 0.0134 gram $\text{CO}_2 = 0.00365$ gram $\text{C} = 0.042$ *per cent. carbon.*

IV. 9.0650 grams phosphorus gave 0.0540 gram $\text{BaSO}_4 = 0.0101$ gram $\text{CO}_2 = 0.00278$ gram $\text{C} = 0.031$ per cent. carbon.

V. 16.4633 grams phosphorus gave 0.1303 gram $\text{BaSO}_4 = 0.0246$ gram $\text{CO}_2 = 0.0067$ gram $\text{C} = 0.041$ per cent. carbon.

VI. 11 grams phosphorus gave 0.0929 gram $\text{BaSO}_4 = 0.0175$ gram $\text{CO}_2 = 0.00478$ gram $\text{C} = 0.043$ per cent. carbon.

The figures speak for themselves. While the absolute quantity of carbon present in the phosphorus is small, it is quite sufficient to account for the results obtained by us in passing air alone over phosphorus, and we consider that the question regarding the action of moist phosphorus on carbon monoxide and air as definitely settled. There is no proof whatever in favor of the view that the carbon monoxide is oxidised. We say this deliberately after having read carefully the last communication of Professor Baumann,¹ in which he states that when air alone is passed over phosphorus it produces no precipitate in baryta water. That is the real point at issue. Upon that we differ diametrically. We invite others to repeat our experiments, and sincerely hope that some may do so.

Contributions from the Chemical Laboratory of Harvard College.

XL.—ON β -BROMTETRACHLORPROPIONIC ACID.

BY CHARLES F. MABERY.

With the hope of establishing the structure of certain bromdichloracrylic acids which I have at present under examination, I endeavored to prepare an acid of the same empirical composition by the addition of a molecule of chlorine to brompropionic acid.²

In studying the relations of these substances toward each other under different conditions, it was found that the action of chlorine upon the melted acid was so violent that frequently it resulted in an explosion. Even at ordinary temperatures a gaseous product

¹ *Berichte der deutschen chemischen Gesellschaft* **17**, 233.

² In a former paper (Mabery and Robinson, this Journal **5**, 255, and *Proceedings Amer. Academy* **18**, 45), it was stated that a bromdichloracrylic acid could be prepared by passing chlorine through a chloroform solution of brompropionic acid cooled to 0°. This statement was evidently made upon insufficient evidence, since all subsequent attempts to obtain the same result have proved unsuccessful.

was freely evolved, with a disagreeable odor resembling that of phosgene.

As previous experiments had shown, in a chloroform solution of the acid the action of chlorine could easily be controlled; in fact, for some time it could not be determined whether the addition had begun, since evaporation of the chloroform left only a pasty mass which refused to crystallise. Finally, after continuing the action for several hours, a crust began to form above the solution, and soon the greater part of a crystalline addition product was deposited.

This substance proved to be sparingly soluble in cold carbonic disulphide and chloroform, more soluble in hot, and after purification it melted with decomposition at 225° . The percentage composition calculated from the results of analysis corresponds to that of bromotetrachloropropionic acid.

I. 0.2000 gram of the substance gave 0.5235 gram $\text{AgBr} + \text{AgCl}$.

II. 0.5874 gram of the substance gave 0.2732 gram CO_2 and 0.0268 gram H_2O .

III. 0.5385 gram of the substance gave 0.2330 gram CO_2 .¹

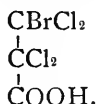
	Calculated for $\text{C}_3\text{HCl}_4\text{BrO}_2$.	I.	Found. II.	III.
C	12.37		12.67	11.82
H	.34		.51	
$4\text{Cl} + \text{Br}$	76.30	76.26		

The salts of this acid are extremely unstable. It dissolves readily in sodic or potassic carbonate, or in ammonic hydrate, and is precipitated by hydrochloric acid; yet the corresponding salts could not be prepared sufficiently pure for analysis. When treated with baric carbonate, the acid dissolves with the formation at first of a clear solution; but soon the latter becomes turbid from the separation of an oil, which continues until the decomposition of the salt is complete. Although this oil was not submitted to analysis, it is probably tetrachlorethylene. The silver salt which is formed when argentic nitrate is brought in contact with the acid, soon changes color, even in the dark, and all attempts to prepare it in a form suitable for analysis were unsuccessful.

Unless a molecular rearrangement takes place during the addi-

¹ By accident the water in this combustion was lost.

tion of chlorine, which does not seem at all probable, the structure of this acid must be represented by the formula :



Many variations of the method of preparation above described have been tried in order, if possible, to limit the addition of chlorine to the formation of a bromdichloracrylic acid. The appearance of the product and its behavior toward solvents at different stages of the chlorination would seem to indicate that each molecule of brompropionic acid absorbed two molecules of chlorine, thereby forming a mixture of bromtetrachlorpropionic acid and unaltered brompropionic. This would, of course, preclude the possibility of obtaining by the addition of chlorine the corresponding substituted acrylic acid.

XLI.—ON *α*- AND *β*-CHLORDIBROMACRYLIC ACIDS.¹

BY CHARLES F. MABERY AND RACHEL LLOYD.

α-CHLORDIBROMACRYLIC ACID.

In a former paper by F. C. Robinson and one of us,² a brief account was given of certain experiments in which we had tried to obtain an addition product of brompropionic acid with chlorine monobromide. Although the results then obtained were rather unsatisfactory, it seemed possible nevertheless to prepare the addition product in a state of purity, and this became especially desirable when it was found that an acid of the same empirical composition could be formed from chlortribrompropionic acid.

In resuming the study of this reaction, it was evidently necessary to secure at the outset a combination of the halogens containing no free bromine, inasmuch as previous results had shown that a small percentage even of tribromacrylic acid could not be removed from the product by crystallisation. On the other hand, an excess of chlorine was not objectionable, since it had been found that this substance in the free state united much less readily with brompro-

¹ The results described in papers XLI, XLII, and XLIII were obtained under my direction in the summer course of instruction in chemistry for 1883.—C. F. M.

² This Journal 5, 254; and Proceedings Amer. Acad. 18, 41.

Angles between Normals.

	Observed.		Calculated.
010 on 100	66° 23'	} Fundamental angles.	
100 " 001	116° 17'		
010 " 001	116° 20'		
100 " 101	63° 50'		
100 " 110	47° 5'		
100 " 430			23° 52'
100 " 740	27°		27° 5'
010 " 470	42° 26'		42° 36'
001 " 034	21°		21°

In the paper above referred to Mr. Huntington makes the following remarks concerning the planes $[430]$, $[0\bar{3}4]$, $[\bar{3}04]$, $[740]$, $[\bar{4}70]$, $[\bar{4}74]$, $[047]$? : "These symbols were for the most part deduced from the zone intersections, and the indices could only in a few cases be verified by angular measurements. The faces of the vertical prism especially were very irregular, in consequence of the alternations caused by parallel grouping, so common with artificial crystals; and although the relative position of the fundamental planes could be accurately fixed, the symbols of the intermediate planes must be regarded as doubtful; these planes were seldom seen, and only in the vertical zone. The symbols given on the projection were obtained by finding the intersection with the vertical zone of other zones never well defined on the same crystal, and it can only be claimed that the approximate angular measurements on the vertical zone were compatible with the indices given above."

The composition of the purified acid was shown by analysis :

I. 0.2254 gram of the substance gave 0.4435 gram $\text{AgCl} + \text{AgBr}$.

II. 0.2046 gram of the substance gave 0.3980 gram $\text{AgCl} + \text{AgBr}$.

III. 0.8187 gram of the substance gave 0.3920 gram CO_2 and 0.0273 gram H_2O . .

	Calculated for $\text{C}_3\text{HCl}_2\text{BrO}_2$.	I.	Found. II.	III.
2Cl + Br	73.91	74.03	73.19	
C	13.56			13.05
H	.38			.37

In determining the solubility of this acid in cold water according

to the method of V. Meyer, a saturated solution was neutralised with baric carbonate, and the barium determined in the filtered solution by precipitation with sulphuric acid.

I. 11.0890 grams of a solution saturated at 20° gave 0.2344 gram BaSO_4 .

II. 1.6299 grams of a solution saturated at 20° gave 0.0379 gram BaSO_4 .

From these results the following percentages were calculated :

I.	II.
5.18	5.68

The barium, calcium, potassium, and silver salts of this acid were prepared and analysed.

Baric α -Chlordibromacrylate, $\text{Ba}(\text{C}_3\text{ClBr}_2\text{O}_2)_{2.3}\text{H}_2\text{O}$. — On saturating an aqueous solution of the acid with baric carbonate a neutral solution was obtained, from which, by evaporation, the barium salt separated in elongated flat prisms with oblique terminations. This salt is much less soluble in cold than in hot water. The crystals which separated from a hot solution were first dried to a constant weight in the air, then heated to 80°.

0.9545 gram of the air-dried salt lost 0.0712 gram H_2O at 80°.

0.8790 gram of the anhydrous salt gave 0.3083 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_3\text{ClBr}_2\text{O}_2)_{2.3}\text{H}_2\text{O}$.	Found.
H_2O	7.46	7.52
	Calculated for $\text{Ba}(\text{C}_3\text{ClBr}_2\text{O}_2)_2$.	
Ba	20.63	20.62

The solubility of the barium salt in cold water was also determined.

I. 1.4307 grams of a solution saturated at 20° gave 0.1190 gram BaSO_4 .

II. 2.5352 grams of a solution saturated at 20° gave 0.2142 gram BaSO_4 .

The results correspond to the following percentages :

I.	II.
20.46	20.70

Calcic α -Chlordibromacrylate, $\text{Ca}(\text{C}_3\text{ClBr}_2\text{O}_2)_{2.2\frac{1}{2}}\text{H}_2\text{O}$. — The calcium salt was prepared by neutralising an aqueous solution of the acid with calcic carbonate. From the concentrated solution the salt separated in irregular branching needles, which lost two

and one half molecules of crystal water at 80°, after drying to constant weight in the air.

I. 1.2644 grams of the air-dried salt lost 0.1006 gram H₂O at 80°.

II. 0.9273 gram of the air-dried salt lost 0.0714 gram H₂O at 80°.

	Calculated for Ca(C ₃ ClBr ₂ O ₂) ₂ 2½ H ₂ O.	I.	Found.	II.
H ₂ O	7.80	7.95		7.70

I. 0.8166 gram of the anhydrous salt gave on ignition with H₂SO₄ 0.2016 gram CaSO₄.

II. 0.8328 gram of the anhydrous salt gave 0.1835 gram CaSO₄.

	Calculated for Ca(C ₃ ClBr ₂ O ₂) ₂ .	I.	Found.	II.
Ca	7.05	7.26		6.47

Potassic α-Chlordibromacrylate, KC₃ClBr₂O₂?—A solution of the aid was carefully neutralised with potassic carbonate, evaporated to a small volume on the water bath, and finally to dryness over sulphuric acid. It formed a deliquescent amorphous crust, in which the potassium was determined after drying at 80°.

1.0508 gram of the salt dried at 80° gave 0.3124 gram K₂SO₄.

	Calculated for KC ₃ ClBr ₂ O ₂ .	Found.
K	12.92	13.36

Argentie α-Chlordibromacrylate, AgC₃ClBr₂O₂. — The silver salt was prepared by the addition of argentic nitrate to an aqueous solution of the barium salt. It separated as a curdy precipitate, which could be recrystallised from hot water without perceptible decomposition. It crystallises in rhombic plates, and is not affected by ordinary daylight.

0.4715 gram of the salt gave 0.1799 gram AgCl.

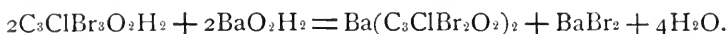
	Calculated for AgC ₃ ClBr ₂ O ₂ .	Found.
Ag	29.07	28.72

β-CHLORDIBROMACRYLIC ACID.

The readiness with which chlortribrompropionic acid is decomposed by alkaline hydrates has already been described,¹ and chlordibromethylen was identified as one of the products when the decomposition was effected with the aid of heat in a strongly alkaline solution.

¹ This Journal 5, 255; and Proceedings Amer. Acad. 18, 45.

A more careful study of the conditions has shown that a halogen atom may be eliminated without severing the connection of the carbon atoms. If the solution is kept cold, and a calculated amount of the alkaline hydrate — by preference baric hydrate — is added slowly, it will retain its acid reaction until the change represented by the following equation is nearly complete :



The solution must then be made slightly alkaline, and kept so for twenty-four hours. On acidifying with hydrochloric acid, the resulting chlordinbromacrylic acid is partially precipitated as an oil, and the remainder may be extracted from the solution with ether.

The acid is purified by crystallisation from hot water, in which it is far more soluble than in cold. It is very soluble in ether and alcohol, less soluble in carbonic disulphide and chloroform. By slow evaporation from a solution in carbonic disulphide it crystallises in oblique prisms, which melt at 99° .

Several attempts were made by Mr. Huntington to determine the crystalline form of this acid in order to compare it with that of α -chlordinbromacrylic acid. But unfortunately all the crystals we were able to obtain for that purpose gave very imperfect reflections, and Mr. Huntington was able to say only that in their general habit they resembled closely those he had already measured of the α -acid. A few planes gave fairly good reflections, and the angles thus measured were nearly the same as those of the α -acid.

	α -Chlordinbromacrylic Acid.	β -Chlordinbromacrylic Acid.	Calculated.
010 on 100	$66^\circ 23'$	67°	
010 " $\bar{4}70$	$42^\circ 26'$	$44^\circ 25'$	
010 " $\bar{7}40$		$42^\circ 26'$	$42^\circ 36'$

The composition of the purified acid was established by analysis.

I. 0.2472 gram of the substance gave 0.4869 gram $\text{AgCl} + \text{AgBr}$.

II. 0.2060 gram of the substance gave 0.4016 gram $\text{AgCl} + \text{AgBr}$.

III. 0.7566 gram of the substance gave 0.3690 gram CO_2 and 0.0325 gram H_2O .

IV. 0.4714 gram of the substance gave 0.2319 gram CO_2 and 0.0227 gram H_2O .

	Calculated for $C_3HClBr_2O_2$.	I.	II. Found.	III.	IV.
Cl + 2Br	73.91	74.09	73.33		
C	13.61			13.30	13.42
H	.38			.48	.54

The solubility of the acid was determined by the method of V. Meyer. After neutralisation with baric carbonate the barium was precipitated from the filtered solution with sulphuric acid.

I. 7.1822 grams of a solution saturated at 20° gave 0.0789 gram $BaSO_4$.

II. 5.3623 grams of a solution saturated at 20° gave 0.0548 gram $BaSO_4$.

From these results the following percentages were calculated :

I.	II.
2.69	2.50

A study of the salts of this acid developed important differences between them and the corresponding salts of *α*-chlordibromacrylic acid.

Baric β-Chlordibromacrylate, $Ba(C_3ClBr_2O_2)_2 \cdot 3H_2O$.—A solution of the acid was heated with an excess of baric carbonate, filtered, and concentrated by evaporation. On cooling, the barium salt crystallised in oblique slender prisms, which were somewhat more soluble in cold water than the barium salt of the *α*-acid. After drying to a constant weight in the air the salt contained three molecules of crystal water, which were slowly given up over sulphuric acid, but more rapidly at 80°.

I. 0.7765 gram of the air-dried salt lost 0.0565 gram H_2O at 80°.

II. 1.0502 grams of the air-dried salt lost 0.0782 gram H_2O at 80°.

III. 0.7185 gram of the anhydrous salt gave 0.2462 gram $BaSO_4$.

IV. 0.5975 gram of the anhydrous salt gave 0.2051 gram $BaSO_4$.

	Calculated for $Ba(C_3ClBr_2O_2)_2 \cdot 3H_2O$.	I.	Found.	II.
H_2O	7.52	7.27		7.45
	Calculated for $Ba(C_3ClBr_2O_2)_2$.	III.		IV.
Ba	20.63	20.15		20.18

In determining the solubility of the barium salt in cold water the following results were obtained :

I. 1.5511 grams of a solution saturated at 20° gave 0.1413 gram BaSO₄.

II. 1.8345 grams of a solution saturated at 20° gave 0.1676 gram BaSO₄.

The solubility of the salt in water at 20° is therefore shown by the following percentages :

I.	II.
25.90	26.04

Calcic β-Chlordibromacrylate, Ca(C₃ClBr₂O₂)₂·4H₂O.—On concentrating a solution of the calcium salt prepared by neutralising a solution of the acid with calcic carbonate, the salt separated in clusters of branching needles, which were less soluble in water than the calcium salt of the α-acid.

I. 1.2644 grams of the air-dried salt lost 0.1345 gram H₂O at 80°.

II. 0.9273 gram of the air-dried salt lost 0.1038 gram H₂O at 80°.

III. 1.2124 grams of the air-dried salt lost 0.1328 gram H₂O at 80°.

IV. 0.8820 gram of the anhydrous salt gave 0.1887 gram CaSO₄.

	Calculated for Ca(C ₃ ClBr ₂ O ₂) ₂ ·4H ₂ O.	I.	Found. II.	III.
H ₂ O	11.27	10.64	11.19	10.91
Ca	Calculated for Ca(C ₃ ClBr ₂ O ₂) ₂ .		6.75	
	7.05			

Potassic β-Chlordibromacrylate, KC₃ClBr₂O₂?—When a solution of the acid was neutralised with potassic carbonate, concentrated on the water bath, and evaporated to dryness over sulphuric acid, the potassium salt was left in the form of a very deliquescent amorphous mass. For analysis the salt was finally dried at 80°.

1.0509 grams of the salt gave 0.4397 gram K₂SO₄.

	Calculated for KC ₃ ClBr ₂ O ₂ .	Found.
K	12.92	12.42

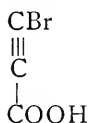
All attempts to prepare a silver salt of this acid were unsuccessful. On the addition of argentic nitrate to a solution of the acid or any of its salts, the solution immediately became turbid from the separation of argentic bromide. This decomposition was not prevented to any appreciable extent by the exclusion of light.

CONSTITUTION OF *α*- AND *β*-CHLORDIBROMACRYLIC ACIDS.

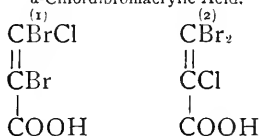
The essential points of difference in the physical properties of these acids, which appear in their general behavior and solubility in water, as well as in their melting points, would seem to point to a difference in structure. In the degree of hydration, solubility in water and comparative stability, their salts exhibit peculiarities as marked as those of the acids themselves. Although the silver salt of the *α*-acid can be prepared without difficulty, the corresponding salt of the *β*-acid cannot be formed even with the greatest care.

While the product obtained by the action of chlorine monobromide upon brompropionic acid may have one of two forms,—

Brompropionic Acid.

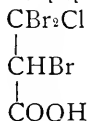


α-Chlordibromacrylic Acid.

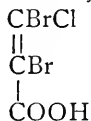


the acid resulting from the abstraction of the elements of hydrobromic acid from chlortribrompropionic acid can evidently have but one:

Chlortribrompropionic Acid.



β-Chlordibromacrylic Acid.



Since the formula of *β*-chlordibromacrylic acid is identical with (1), the structure of the *α*-acid is probably represented by (2); or during the addition of chlorine monobromide to brompropionic acid, the weaker halogen unites with the terminal carbon atom.

XLII.—ON *β*-DIBROMDICHLORPROPIONIC AND *β*-BROMDICHLORACRYLIC ACIDS.

BY CHARLES F. MABERY AND H. H. NICHOLSON.

β-DIBROMDICHLORPROPIONIC ACID.

In a brief examination of the action of chlorine on *β*-dibromacrylic acid, it was found by F. C. Robinson and one of us,¹ that, although

¹ This Journal 5, 254; and Proceedings Amer. Acad. 18, 44.

the acid was not affected at ordinary temperatures, an addition-product could readily be obtained by raising the temperature. Further study of this reaction shows that the most desirable results are obtained as regards time, as well as the quality and quantity of the product, if the temperature is kept near 100° . In one experiment, after continuing the action for eight hours, 5.9 grams β -dibromacrylic acid gave 7.9 grams of the crude β -dibromdichlorpropionic acid, which melted without purification above 90° , or ninety-six per cent. of the amount of pure acid theoretically required.

The crude acid was easily purified by two or three crystallisations from a hot solution in carbonic disulphide, which deposited the greater part of the acid when cooled to 0° . It is but sparingly soluble in water, more soluble in hot than in cold chloroform, and very soluble in ether and alcohol. It crystallises in oblique prisms, which melt at 100° and sublime slowly at higher temperatures. The composition of this acid was determined by the following analyses:

I. 0.2142 gram of the substance gave 0.4712 gram AgCl + AgBr.

II. 0.8223 gram of the substance gave 0.3485 gram CO_2 and 0.0510 gram H_2O .

	Calculated for $\text{C}_3\text{H}_2\text{Cl}_2\text{Br}_2\text{O}_2$.	Found.	
		I.	II.
Cl + Br	76.74	76.67	
C	11.96		11.55
H	.66		.69

The salts of this acid are comparatively unstable. We were unable to prepare a silver salt in a form suitable for analysis, since argentic bromide began to separate as soon as argentic nitrate came in contact with the acid. Although there was no perceptible decomposition of the acid when it was treated in the cold with baric carbonate, several different preparations of the salt proved on analysis to contain a quantity of barium nearly three per cent. in excess of the calculated value. In the preparation of the calcium and potassium salts we found less difficulty.

Calcic β -Dibromdichlorpropionate, $\text{Ca}(\text{C}_3\text{Cl}_2\text{Br}_2\text{O}_2\text{H}) \cdot 1\frac{1}{2}\text{H}_2\text{O}$.—On treating the acid with calcic carbonate and calcic hydrate in the cold, filtering, and concentrating by spontaneous evaporation at the ordinary temperature, the calcium salt separated in clumps of needles. After drying to a constant weight in the air the salt lost one and a half molecules of crystal water at 80° .

I. 0.7775 gram of the air-dried salt lost 0.0307 gram H_2O at 80° .

II. 0.9392 gram of the anhydrous salt lost 0.0403 gram H_2O at 80° .

III. 0.8626 gram of the anhydrous salt gave 0.1796 gram $CaSO_4$.

	Calculated for $Ca(C_3HCl_2Br_2O_2)_2 \cdot \frac{1}{2}H_2O$.	I.	Found.	II.
H_2O	4.05	3.95		4.29
	Calculated for $Ca(C_3HCl_2Br_2O_2)_2$.			
Ca	6.25		6.13	

Potassic β-Dibromdichlorpropionate, $K(C_3HCl_2Br_2O_2)_2 \cdot 2H_2O$.—The potassium salt was made by neutralising the acid with an aqueous solution of potassic carbonate and allowing it to evaporate without the application of heat. The air-dried salt contained two molecules of crystal water, which it lost over sulphuric acid.

I. 0.8735 gram of the air-dried salt lost 0.0809 gram H_2O over H_2SO_4 .

II. 0.7933 gram of the anhydrous salt gave 0.2171 gram K_2SO_4 .

	Calculated for $KC_3HCl_2Br_2O_2 \cdot 2H_2O$.	Found.
H_2O	9.66	9.26
	Calculated for $KC_3HCl_2Br_2O_2$.	
K	11.53	12.28

β-BROMDICHLORACRYLIC ACID.

β-dibromdichlorpropionic acid is readily decomposed by alkaline hydrates, and when the reaction is allowed to progress in the cold, the elements of hydrobromic acid are eliminated with the formation of the corresponding substituted acrylic acid. The best results were obtained by treating the acid with an aqueous solution of baric hydrate in slight excess over the calculated amount, and keeping the solution slightly alkaline for twenty-four hours. Upon acidifying this solution with hydrochloric acid, dichlorbromacrylic acid was partially precipitated as an oil, which solidified when cooled to 0° . Since the acid is quite soluble in water, the solution was extracted with ether, and the total product was purified by several crystallisations from hot water.

This acid is very soluble in hot, rather sparingly soluble in cold water, and very soluble in carbonic disulphide, chloroform, ether, and alcohol. It crystallises from water in large pearly scales, which melt at 75° – 78° . Its composition was determined by analysis.

I. 0.2374 gram of the substance gave 0.5059 gram $\text{AgCl} + \text{AgBr}$.

II. 0.2034 gram of the substance gave 0.4377 gram $\text{AgCl} + \text{AgBr}$.

III. 0.7255 gram of the substance gave 0.4433 gram CO_2 and 0.0337 gram H_2O .

	Calculated for $\text{C}_3\text{HCl}_2\text{BrO}_2$.	I.	Found. II.	III.
$2\text{Cl} + \text{Br}$	68.64	67.76	68.42	
C	16.36			16.66
H	.46			.52

In determining the solubility of this acid in cold water, a solution saturated at 20° was neutralised with baric carbonate, and the barium was determined in the filtered solution.

I. 6.0061 grams of a solution saturated at 20° gave 0.1523 gram BaSO_4 .

II. 7.4519 grams of a solution saturated at 20° gave 0.1872 gram BaSO_4 .

From these results the following percentages were calculated :

I.	II.
4.79	4.74

This acid is characterised by a series of well-defined salts, several of which were prepared for analysis.

Baric β -Bromdichloracrylate, $\text{Ba}(\text{C}_3\text{Cl}_2\text{BrO}_2)_2 \cdot 3\text{H}_2\text{O}$.—The barium salt was made by neutralising the acid in aqueous solution with baric carbonate. It separated after concentration on the water bath in prismatic crystals, which were less soluble in cold than in hot water.

I. 1.3622 grams of the air-dried salt lost at 80° 0.1162 gram H_2O .

II. 1.2529 grams of the air-dried salt lost at 80° 0.1046 gram H_2O .

III. 0.5757 gram of the anhydrous salt gave 0.2353 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_3\text{Cl}_2\text{BrO}_2)_2 \cdot 3\text{H}_2\text{O}$.	I.	Found. II.
H_2O	8.58	8.53	8.35
	Calculated for $\text{Ba}(\text{C}_3\text{Cl}_2\text{BrO}_2)_2$.	III.	
Ba	23.82	24.03	

Calcic β -Bromdichloracrylate, $\text{Ca}(\text{C}_3\text{Cl}_2\text{BrO}_2)_2 \cdot 3\text{H}_2\text{O}$.—The calcium salt separated in the form of rhombic plates sparingly soluble in cold water, when an aqueous solution of the acid was neutralised with calcic carbonate and concentrated on the water bath. For

analysis it was dried first at a constant weight in the air, then at 80°.

- I. 1.2318 grams of the salt gave 0.1195 gram H₂O at 80°.
II. 1.1054 grams of the salt gave 0.1088 gram H₂O at 80°.
III. 0.9719 gram of the anhydrous salt gave 0.2741 gram CaSO₄.

	Calculated for Ca(C ₃ Cl ₂ BrO ₂) ₂ ·3H ₂ O.	I.	Found.	II.
H ₂ O	10.15	9.71		9.85
	Calculated for Ca(C ₃ Cl ₂ BrO ₂) ₂ .		III.	
Ca	8.37		8.29	

Potassic β-Bromdichloracrylate, KC₃Cl₂BrO₂.—The potassium salt was prepared by neutralisation of the acid with potassic carbonate. After concentrating the solution the salt separated in minute prismatic crystals, which were very soluble in water. When dried to a constant weight in the air, it lost nothing at 80°.

1.2362 grams of the salt dried at 80° gave 0.4144 gram K₂SO₄.

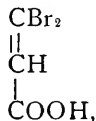
	Calculated for KC ₃ Cl ₂ BrO ₂ .	Found.
K	15.15	15.03

Argentich β-Bromdichloracrylate, AgC₃Cl₂BrO₂.—The silver salt was thrown down as a flocculent precipitate upon the addition of argentic nitrate to an aqueous solution of the acid. This salt is permanent in ordinary daylight, and it can be recrystallised from hot water without decomposition. It forms irregular rhombic plates, which are very slightly soluble in cold water.

0.6191 gram of salt dried over H₂SO₄ gave 0.2660 gram AgCl.

	Calculated for AgC ₃ Cl ₂ BrO ₂ .	Found.
Ag	33.03	32.34

Since β-dibromacrylic acid has been shown¹ to have the structure represented by the formula,

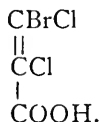


the chlorine addition-product would naturally have the form,



¹ H. B. Hill, this Journal **4**, 273; and Proceedings Amer. Acad. **17**, 151.

and to the corresponding β -bromdichloracrylic acid must be assigned the formula,



XLIII.—ON ORTHOIODTOLUOLSULPHONIC ACID.

BY CHARLES F. MABERY AND GEORGE H. PALMER.

Hübner and Glassner¹ found that, when paraiodtoluol was dissolved in chloroform and treated with the calculated amount of sulphuric anhydride, two acids were formed, which they called α - and β -paraiodsulfitoluols. On trying the same reaction with orthoiodtoluol prepared from orthotoluidin by means of the diazo reaction, we were unable to effect any change in a chloroform solution, either in the cold or by the application of heat. But when sulphuric anhydride freshly distilled from Nordhausen sulphuric acid was added cautiously to the iodtoluol, at first keeping the mixture cold, and finally heating it for some time, the reaction was easily accomplished. To separate the resulting product from the acid mixture it was treated with an excess of baric carbonate, heated to boiling, filtered, and concentrated on the water bath. On cooling, the barium salt of orthoiodtoluolsulphonic acid separated in clusters of needles, which were much less soluble in cold than in hot water. So far as it could be determined by any difference in solubility or crystalline form of the barium salt, only one acid was formed. By precipitating carefully with sulphuric acid the barium from a solution of the barium salt, and concentrating the filtered solution on the water bath, the acid was left as an oily liquid, which did not solidify when cooled to 0° , or on long standing over sulphuric acid.

Baric Orthoiodtoluolsulphonate, $\text{Ba}(\text{C}_7\text{H}_6\text{ISO}_3)_2 \cdot 1\frac{1}{2} \text{H}_2\text{O}$.—For analysis the barium salt was prepared as above described, and dried at first in the air, then at 100° .

I. 1.2312 grams of the air-dried salt lost 0.0407 gram H_2O at 100° .

II. 0.8011 gram of the air-dried salt lost 0.0300 gram H_2O at 100° .

¹ Berichte der deutschen chem. Gesellsch. **8**, 560.

III. 0.5967 gram of the anhydrous salt gave 0.1888 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_7\text{H}_6\text{ISO}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$.	I.	Found. II.
H_2O	3.54	3.31	3.66
Ba	Calculated for $\text{Ba}(\text{C}_7\text{H}_6\text{ISO}_3)_2$. 18.61		18.03

Calcic Orthoiodtoluolsulphonate, $\text{Ca}(\text{C}_7\text{H}_6\text{ISO}_3)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$.—This salt was prepared by neutralising the free acid with calcic carbonate, and evaporating the filtered solution on the water bath. The air-dried salt was heated to 100° .

I. 0.6243 gram of the air-dried salt lost 0.0414 gram H_2O at 100° .

II. 0.6250 gram of the air-dried salt lost 0.0424 gram H_2O at 100° .

	Calculated for $\text{Ca}(\text{C}_7\text{H}_6\text{ISO}_3)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$.	I.	Found. II.
H_2O	6.62	6.61	6.78

0.7298 gram of the anhydrous salt gave 0.1762 gram CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_7\text{H}_6\text{ISO}_3)_2$.	Found.
Ca	6.31	7.10

Plumbic Orthoiodtoluolsulphonate, $\text{Pb}(\text{C}_7\text{H}_6\text{ISO}_3)_2 \cdot 2\text{H}_2\text{O}$.—The lead salt was formed by treating the free acid with plumbic carbonate, filtering, and evaporating on the water bath. The air-dried salt lost two molecules of crystal water at 100° .

I. 1.2580 grams of the air-dried salt lost 0.0562 gram H_2O at 100° .

II. 1.2538 grams of the air-dried salt lost 0.0512 gram H_2O at 100° .

III. 0.7176 gram of the air-dried salt lost 0.0294 gram H_2O at 100° .

IV. 0.6163 gram of the anhydrous salt gave 0.2318 gram PbSO_4 .

V. 0.6455 gram of the anhydrous salt gave 0.2425 gram PbSO_4 .

	Calculated for $\text{Pb}(\text{C}_7\text{H}_6\text{ISO}_3)_2 \cdot 2\text{H}_2\text{O}$.	I.	Found. II.	III.
H_2O	4.30	4.47	4.01	4.10
Pb	Calculated for $\text{Pb}(\text{C}_7\text{H}_6\text{ISO}_3)_2$. 25.78	V. 25.75	VI. 25.72	

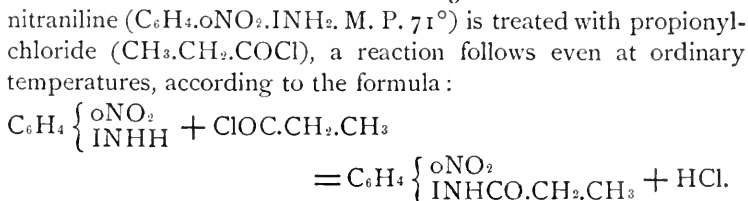
An analysis of the free acid gave a percentage of iodine somewhat lower than the calculated value, but further study of it was prevented by the closing of the summer term.

ON THE ACTION OF BROMINE ON ANHYDROPRO- PIONYLPHENYLENDIAMINE.

BY ERASTUS G. SMITH.

The anhydrobase anhydropropionylphenylendiamine was first prepared and briefly described by Wundt (Berichte der deutschen chemischen Gesellschaft **II**, 829). The base has been prepared by the writer by another method, and several new salts of the same obtained. The method of preparation, and the preparation and analyses of the new salts, together with some corrections to those already described, are here given.

Ortho-nitro-propanilide, $C_6H_4 \left\{ \begin{array}{l} oNO_2 \\ INH.CO.CH_2.CH_3 \end{array} \right.$ —If ortho-nitraniline ($C_6H_4.oNO_2.INH_2$, M. P. 71°) is treated with propionylchloride ($CH_3.CH_2.COCl$), a reaction follows even at ordinary temperatures, according to the formula :



The operation is best carried out as follows : The orthonitraniline is introduced into a short-necked flask with a standing tube, and somewhat more than the reckoned amount of the propionylchloride added. The reaction follows immediately, but it is best to warm gently to insure completeness. The fused mass is extracted with alcohol, and purified by recrystallisation to constant melting point. The ortho-nitro-propanilide thus obtained melts at $63^\circ C.$ and crystallises from its solutions in large lemon-yellow crystals. It is soluble in boiling water, in alcohol, ether, and benzole.

Nitrogen Determination.—1.785 gram of the dried crystals yielded 21.6 cc. N at $7^\circ C.$ and under 752 mm. pressure = 14.53 per cent. N.

	Reckoned.	Found.
$C_9H_{10}O_3$	85.55 per cent.	
N_2	14.43 "	14.53 per cent.

Anhydro-propionyl-phenylendiamine, $C_6H_4 \left\{ \begin{array}{l} N \\ > \\ NH \end{array} \right. C.CH_2.CH_3$.—
M. P. $168^\circ C.$

If ortho-nitro-propanilide is treated with reducing agents, preferably tin and glacial acetic acid, this anhydrobase is formed. In the present case, at the close of the reaction the excess of tin was removed and the liquid poured into 5-6 volumes of water. The greater part of the tin was thus precipitated, and the remainder removed by sulphuretted hydrogen. The liquid was evaporated nearly to dryness and finally distilled in a small retort. For purification it is best to dissolve in hydrochloric acid and recrystallise. From this salt the pure base is precipitated by soda. The anhydropropionyl-phenylen-diamine is easily soluble in benzole, ether, alcohol, and boiling water, the solution from benzole depositing needle-shaped crystals. Its melting point is 168° C.

Analyses.

I. .2005 gram of the base yielded 33.1 cc. N at 10.5° C. and under 753.5 mm. pressure = 19.56 per cent. N.

II. .3771 gram of the dry base yielded 1.035 grams CO₂ = 74.16 per cent. C, and .2335 gram H₂O = 6.88 per cent. H.

	Reckoned.	Found.
C ₉	73.97 per cent.	74.16 per cent.
H ₁₀	6.84 “	6.88 “
N ₂	19.17 “	19.56 “

The base gives a series of well crystallising salts, *none of them containing water of crystallisation*.¹

I. *Hydrochloric Acid Salt*, C₆H₄ $\left\{ \begin{array}{l} \text{N} \\ \text{>C.CH}_2\text{.CH}_3 \\ \text{NH}_2\text{Cl} \end{array} \right.$ —If the an-

hydrobase is dissolved in water and HCl added, the solution yields by evaporation long colorless crystals of the hydrochloric acid salt *without water of crystallisation*.

Analysis.

.1064 gram of the salt yielded .0841 gram Ag₂Cl₂ = 19.54 per cent. Cl.

	Reckoned.	Found.
C ₆ H ₁₁ N ₂	80.53 per cent.	
Cl	19.45 “	19.54 per cent.

II. *Platinum Chloride Double Salt*,



¹ Ber. d. chem. Ges. 11, 829.

If to the solution of the hydrochloric acid salt, platinum chloride is added in excess, the solution yields on evaporation bright orange red crystals of the platinum chloride double salt. *These crystals contain no water of crystallisation.*

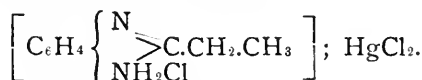
Analyses.

I. .3374 gram of the salt yielded on ignition .0944 gram = 27.98 per cent. Pt.

II. From 1.14885 grams of the salt the platinum precipitated as PtS_2 and ignited, gave .3211 gram = 27.93 per cent. Pt.

	Reckoned.	I.	Found.	II.
$\text{C}_{18}\text{H}_{22}\text{N}_4\text{Cl}_2\text{Cl}_4$	72.26 per cent.			
Pt	27.73 “	27.98 per cent.		27.93 per cent.

III. *Mercuric Chloride Double Salt,*



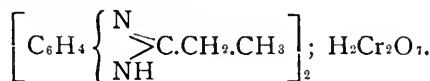
If mercuric chloride is added to the hydrochloric acid salt and the solution evaporated, the mercuric chloride double salt crystallises out in long colorless needles.

Analysis.

.516 gram of the salt yielded with sulphuretted hydrogen .2864 gram HgS = 44.19 per cent. Hg.

	Reckoned.	Found.
$\text{C}_6\text{H}_{11}\text{N}_2\text{Cl}_3$	55.74 per cent.	
Hg	44.15 “	44.19 per cent.

IV. *Pyrochromic Acid Salt,*



If about two grams of the base are dissolved in sulphuric acid and $\text{K}_2\text{Cr}_2\text{O}_7$ added, this salt is obtained on evaporating the solution.

Analysis.

.1683 gram of the salt gave .0511 gram Cr_2O_3 = 20.79 per cent. Cr.

	Reckoned.	Found.
$\text{C}_{18}\text{H}_{22}\text{N}_4\text{O}_7$	79.45 per cent.	
Cr_2	20.54 “	20.79 per cent.

The Action of Bromine on Anhydropropionylphenyldiamine.

It is possible by this action to effect, either:

a. The substitution of bromine for hydrogen in the phenylene group (C_6H_4), or:

b. An oxidation whereby the anhydrobase can be changed to a carboxyl compound, or:

c. Both reactions could simultaneously occur.

It will be shown that the bromine substitutions are undoubtedly effected. And from investigations yet in progress there are strong reasons for believing that by the continued action of bromine an oxidation of the bromine bases actually takes place. The treatment with the bromine is as follows:

Twenty grams of the pure anhydrobase are dissolved in two litres of hot water, and, after cooling, diluted bromine water is added in small portions until the color of the bromine water after standing twelve hours is distinctly permanent. A heavy, difficultly soluble, flocculent precipitate is formed. What has dissolved can be advantageously precipitated by sodium acetate and the whole filtered and well washed with *cold* water. The white mass thus obtained is dissolved in alcohol and allowed to crystallise. At first thick yellow crystals separate, and after longer standing, *long colorless needles* appear. Immediately on their appearance the mother liquor is filtered off and the crystals washed with dilute alcohol, and finally with a little dilute hydrochloric acid and cold water. The further treatment must proceed in two parts:

a. The alcoholic mother liquor.

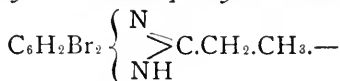
b. The insoluble crystals.

a. To the alcoholic mother liquor is added an excess of hydrochloric acid and the whole evaporated on the water bath. On standing the hydrochloric acid salt of the base anhydro-propionyl-di-bromine-phenylen-diamine crystallises out.

b. The insoluble crystals when boiled with barium hydroxide are partially dissolved. The insoluble portion is filtered off and dissolved in alcohol. After again filtering to free from traces of barium carbonate, the solution yields on evaporation the nearly pure crystalline base anhydro-propionyl-tri-bromine-phenylen-diamine. The portion soluble in barium hydroxide is evaporated with hydrochloric acid to dryness, and extracted with alcohol. This alcoholic extract evaporated, redissolved in water and treated with sodium acetate, gives a precipitate crystallising well from

alcohol. This appears to possess the properties of an acid, but has not yet been fully investigated.

Anhydropropionyl-di-bromine-phenylen-diamine,



M. P. 224–226° C.

The hydrochloric acid salt described above (*a*) is thrice recrystallised and the pure base precipitated with ammonia. The white flocculent precipitate is difficultly soluble even in boiling water, but dissolves readily in benzole, ether, *dilute* alcohol and *strong caustic soda*. The crystals from alcohol melt at 224–226° C. The complete analysis will be given below under the nitric acid salt.

Nitric Acid Salt, $\text{C}_6\text{H}_2\text{Br}_2 \left\{ \begin{array}{l} \text{N} \\ \text{>} \\ \text{NH}_2\text{ONO}_2 \end{array} \right. \text{C}.\text{CH}_2.\text{CH}_3.-$ A gram of the

pure base dissolved in water and treated with nitric acid yields on evaporation crystals of the nitric acid salt. These are especially fine and well adapted for complete analysis to fully establish the composition of the base.

Analyses.

I. .1745 gram of the salt gave 17.6 cc. N at 16° C. and under 747 mm. pressure = 11.55 per cent. N.

II. .1795 gram of the salt yielded .0447 gram H_2O = 2.73 per cent. H, and .1924 gram CO_2 = 29.23 per cent. C.

III. .192 gram of the salt heated to 180° C. with HNO_3 and silver nitrate gave .1989 gram Ag_2Br_2 = 44.04 per cent. bromine.

	Reckoned.	Found.
C_9	29.42	29.23
H_9	2.45	2.73
Br_2	43.59	44.04
N_3	11.44	11.55
O_3	13.08	

Hydrochloric Acid Salt, $\text{C}_6\text{H}_2\text{Br}_2 \left\{ \begin{array}{l} \text{N} \\ \text{>} \\ \text{NH}_2\text{Cl} \end{array} \right. \text{C}.\text{CH}_2.\text{CH}_3; \text{H}_2\text{O}.-$

This salt is obtained in long acicular crystals, as already given in the preparation of the base.

Analyses.

I. The salt contains one molecule of water of crystallisation.

The water cannot however be expelled without decomposing the salt. .7232 gram remained constant at 152° C. Between 152–155° the salt is decomposed.

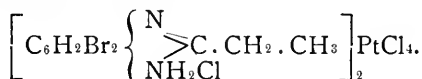
II. .21975 gram of the salt gave .084 gram $\text{Ag}_2\text{Cl}_2 = 9.45$ per cent. Cl.

III. .20515 gram of the salt gave .0792 gram $\text{Ag}_2\text{Cl}_2 = 9.51$ per cent. Cl.

IV. .1739 gram of the salt gave .07009 gram $\text{Ag}_2\text{Cl}_2 = 9.96$ per cent. Cl.

	Reckoned.	I.	Found. II.	III.
$\text{C}_9\text{H}_9\text{Br}_2\text{N}_2;\text{H}_2\text{O}$	90.09 per cent.			
Cl	9.90	“ 9.45 per ct.	9.51 per ct.	9.96 per ct.

Platinum Chloride Double Salt,



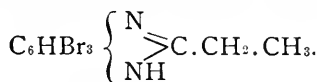
A gram of the hydrochloric acid salt dissolved in water and platinum chloride added, gives fine orange-red crystals of the platinum double salt.

Analysis.

From .1935 gram of the salt the platinum precipitated as PtS_2 and ignited, gave .0358 gram = 19.04 per cent. Pt.

	Reckoned.	Found.
$\text{C}_{18}\text{H}_{18}\text{Br}_4\text{N}_4\text{Cl}_2\text{Cl}_4$	80.90 per cent.	
Pt	19.09	“ 19.04 per cent.

Anhydropropionyl-tri-bromine-phenylen-diamine,



M. P. 257–262° C.

The preparation of this base has been already given under *b*. The pale yellow granular crystals are difficultly soluble in alcohol, ether, benzole, and hot water. Crystals from alcohol melt at 257–262° C.

Analyses.

I. .2126 gram of the base gave 14 cc. N at 25° C. and under 751 mm. pressure = 7.25 per cent. N.

II. .1013 gram of the crystals gave .1031 gram $\text{CO}_2 = 27.75$ per cent. C, and .0286 gram $\text{H}_2\text{O} = 3.06$ per cent. N.

III. .1804 gram of the base gave (when heated to 180°C . with nitric acid and silver nitrate) .2166 gram $\text{Ag}_2\text{Br}_2 = 62.86$ per cent. Br.

	Reckoned.	Found.
C_9	28.19	27.75
H_7	1.82	3.06
N_2	7.31	7.25
Br_3	62.63	62.86

Hydrochloric Acid Salt, $\text{C}_9\text{HBr}_3 \left\{ \begin{array}{l} \text{N} \\ \text{NH}_2 \cdot \text{Cl} \end{array} \right. \text{C} \cdot \text{CH}_2 \cdot \text{CH}_3; 2\text{H}_2\text{O}$. — If

the base is dissolved in dilute hydrochloric acid and the solution evaporated, this salt is obtained in small transparent crystals.

Analyses.

I. .1227 gram of the air-dried crystals lost at 100° .009 gram = 7.33 per cent. H_2O .

	Reckoned.	Found.
$\text{C}_9\text{H}_7\text{Br}_3\text{N}_2, \text{HCl}$	92.09 per cent.	
H_2O	7.90 “	7.33 per cent.

II. .114 gram of the anhydrous salt yielded .0942 gram $\text{Ag}_2\text{Cl}_2 = 8.26$ per cent. Cl.

	Reckoned.	Found.
$\text{C}_9\text{H}_7\text{Br}_3\text{N}_2, \text{H}$	91.53 per cent.	
Cl	8.46 “	8.26 per cent.

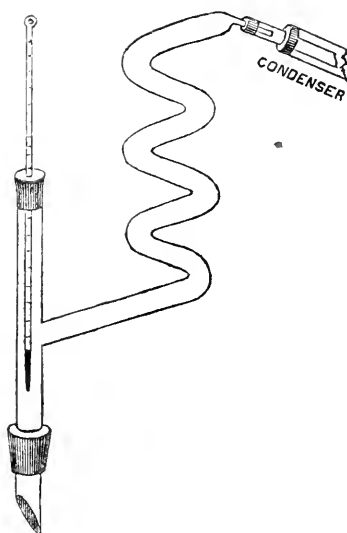
CHEMICAL LABORATORY OF BELOIT COLLEGE, *Beloit, Wisconsin*.

NEW FORMS OF LABORATORY APPARATUS.

BY EDWARD HART.

I.—*Apparatus for Fractional Distillation.*

The apparatus has the form shown in the figure. The bent tube before bending should be at least 2 feet long, but may be of any

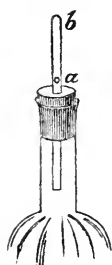


length with a corresponding number of bends (the greater the length, the more perfect the separation), and an internal diameter of at least $\frac{3}{8}$ inch. The principle is the familiar one of the "dephlegmator." The condensed portion here runs down, and at each bend passes around the inside of the tube, the vapor passing upward through the ring of descending liquid. A comparison with a Le Bel and Henniger tube¹ with 4 bulbs showed very little difference in the rate of separation. The apparatus is preferable to that of Le Bel and Henniger by reason of its simplicity and small cost. It

can be made by an amateur glassblower, while the former can be made only by a skilled workman.

II.—A Valve for use in Standardising Permanganate.

The valve shown has been in use for several years in this laboratory, and proves perfectly satisfactory. The trouble with the old forms (in one of which a slit is made in the side of a rubber tube, and in the second, a piece of rubber is pinned over a hole in a cork, and this slipped over a tube leading from the flask) is that

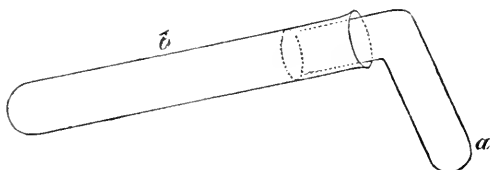


however carefully they are made, they get out of order very soon and become a nuisance. The liquid in the flask is rapidly heated as soon as the iron wire is introduced, and as soon as the wire is dissolved, boiled to expel all air, and the tube pushed down so that the opening *a* in the tube is inside the opening of the rubber cork, which prevents the air from flowing back into the flask as it cools. The tube is closed at *b*. The opening *a* is made either by filing crosswise with a rat-tail file, or better, by heating with a pointed flame and blowing an opening in the side of the tube.

¹ Berichte d. deut. chem. Ges. 7, 1084.

III.—*A Retort and Receiver for small Distillations.*

It is oftentimes inconvenient to use a retort in making small distillations, chiefly because it takes considerable time to fit up a retort stand. For such small distillations as the preparation of chlorochromic acid in testing for chlorine, the following arrangement is convenient :



The retort tube *a* is made by bending a 6 inch test tube. If the tube is heated to redness and blown into while bending, a neat and strong bend is easily made. In use, the receiver tube *b* is held in the hand while the retort tube is placed above a small flame. For a retort tube made from a 4 inch test tube, a 6 inch test tube makes a receiver of the proper size. For a 6 inch retort tube an 8 inch test tube is needed.

LAFAYETTE COLLEGE, *April*, 1884.

ON A NEW CLASS OF COMPOUNDS ANALOGOUS TO THE PHTHALEINS.

BY IRA REMSEN.

The analogy in constitution between phthalic and ortho-sulphobenzoic acids suggested that the latter might act upon phenols in the same way that the former does, and that thus compounds analogous to the phthaleins might be obtained. Experiment showed that this thought is well founded. A mixture of about equal parts of pure potassium ortho-sulphobenzoate and resorcin was brought into a dry test-tube with a small quantity of concentrated sulphuric acid, and the whole gently heated for a few minutes. A drop of the resulting dark-colored liquid was dissolved

in a test-tube full of water and a little caustic soda added, when a fluorescence fully equal to that caused by ordinary fluorescein was observed. By transmitted light the color of the solution is somewhat redder than that of fluorescein, but in other respects they can hardly be distinguished from one another. The same reaction takes place and with the same ease, when instead of the salt of ortho-sulphobenzoic acid, the imide derivative, benzoic

sulphinide, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{SO}_2 \end{smallmatrix} > NH$, is used.

Substitution products of ortho-sulphobenzoic acid act in the same way. The experiment has been tried with nitro-ortho-sul-

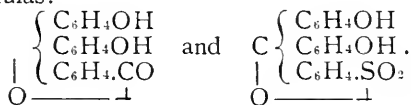
phobenzoic acid, $C_6H_3 \begin{smallmatrix} \text{COOH} \\ \text{SO}_2\text{OH} \text{ (} o \text{)} \\ \text{NO}_2 \text{ (} p \text{)} \end{smallmatrix}$, readily obtained by oxidising

the corresponding nitro-toluenesulphonic acid, and brom-ortho-

sulphobenzoic acid, $C_6H_3 \begin{smallmatrix} \text{COOH} \\ \text{SO}_2\text{OH} \text{ (} o \text{)} \\ \text{Br (} p \text{)} \end{smallmatrix}$, obtained from brom-tolu-

enesulphonic acid.

It is probable that the simplest phthalein prepared in this way will be found to bear to phenol-phthalein the relation indicated by these formulas:



The compounds may appropriately be designated as *sulphon-phthaleins*, which distinguishes them from the normal phthaleins of Baeyer and the thio-phthaleins the formation of which from

thio-phthalic anhydride, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CS} \end{smallmatrix} > O$, and the phenols has been

made probable by the experiments of Graebe.¹

Experiments, which it is hoped will lead to a more definite knowledge of the sulphon-phthaleins, have been undertaken in this laboratory. As, on account of the vacation, nothing more can be done on the subject until next fall, I have thought it desirable at this time to call attention to the reaction. Should it prove possible to isolate the new bodies, I propose, with the aid of some of my younger colleagues, to make an exhaustive study of them.

¹ Berichte der deutschen chemischen Gesellschaft 17, 1177.

THE DECOMPOSITION OF SULPHONIC ACIDS BY HEATING WITH HYDRATED SULPHURIC ACID.

BY C. FRIEDEL AND J. M. CRAFTS.

Messrs. Armstrong and Miller give, in the last numbers of the *Journal of the Chemical Society*, a method for regaining aromatic hydrocarbons from their sulphonic acids, by distilling these latter, mixed with sulphuric acid more or less diluted, in a current of steam, or by heating the mixture in sealed tubes at various temperatures.

They have also succeeded in separating certain hydrocarbons by taking advantage of the differences of temperature at which their sulphonic acids are decomposed.

This publication leads us to speak of experiments in the same direction which entirely confirm the observations of these authors, and bear witness to the great convenience of their method. We have employed, for two years past, exactly the same process for decomposing the sulphonic acids of a class of bodies which cannot be separated from that combination by hydrochloric acid; namely, the sulphonic acids of the hydrides of naphthalene. The publication of the results was, however, delayed, because these compounds were found to present not only this difficulty, for their isolation in a state of purity, but also the more serious one of being readily oxidisable in the air,¹ and this latter property has prevented us

¹In the month of September of last year, one of us communicated to Professor Graebe the fact of the easy oxidation in the air of the tetrahydride of naphthalene, obtained by the decomposition of naphthalene with chloride of aluminium. Graebe had taken up the study of the tetrahydride formed by the action of iodhydric acid upon naphthalene, but he was not aware at that time that this body was oxidisable in the air, and thought the tetrahydrides formed in these two reactions might be distinct bodies. He has since published, together with Mr. Guye (Chem. Gesell., Dec. 1883), some observations upon this subject, which show that in this respect there is no distinction between the hydrides of naphthalene formed by the chloride of aluminium or by the iodhydric acid process, but it still remains to be seen whether the two products are really identical.

The tetrahydride of naphthalene, which we had in hand, was found to form at least two sulphonic acids, but they are oxidisable in the air, as well as their salts, in aqueous solution; and the solubility of the salts is seen to change rapidly when their solutions are exposed to evaporation. In order, therefore, to get their true coefficient of solubility, it will be necessary to evaporate them in an atmosphere of an inert gas.

It is impossible to make a comparison with the sulpho salt of the acid studied by Messrs. Graebe and Guye, as they give no determinations of solubility. The principal product, which can be obtained by treatment with hydrated sulphuric acid after such an oxidation, is naph-

thus far from being able to obtain salts of these acids in a satisfactory condition. The study of these substances is in progress, and we had intended to publish an account of the mode of decomposition of their sulphonic acids as part of a paper upon the hydrides of naphthalene and other bodies which can be obtained by decomposing naphthalene with chloride of aluminium, but as the results are incomplete, we will speak of the interesting decompositions of the sulphonic acids which we have observed.

The tetrahydride of naphthalene combines very readily with strong sulphuric acid at the ordinary temperature, with considerable disengagement of heat, and the resultant sulphonic acid is a very stable body. It only begins to be decomposed by heating with chlorhydric acid at 185° , and at this temperature, decomposition takes place, and the products formed are naphthalene and sulphuretted hydrogen mixed with more or less of the hydride. The reduction of sulphuric acid by a hydrocarbon of this class has, we believe, not hitherto been observed.

It was in order to avoid this decomposition that we adopted the expedient, at first, of heating the sulphonic acid or its salt in sealed tubes, in an essence of turpentine bath (157°), with a mixture of sulphuric acid and various proportions of water, from one half to three times the weight of the sulphuric acid. Total decomposition is effected in about 12 hours, and no oxidation takes place. The rapidity of the decomposition increases, within certain limits, with the strength of the sulphuric acid; an aqueous solution of the sulphonic acid, for instance, is entirely stable when heated at 157° . The range of temperature appeared to be from about 145° to 160° , at which sulphuric acid of the different strengths mentioned decomposed the hydride of naphthalene sulphonic acid.

We worked with large quantities, more than a kilogram, of hydride of naphthalene, and in many cases found it more convenient to use exactly the process of distillation with steam which

thalene, and on decomposing the sulphonic acids at any stage, mixtures of hydride of naphthalene and of naphthalene were the only bodies obtained.

The hydrocarbon itself, when exposed several months in a loosely corked flask, absorbs oxygen and undergoes a transformation similar to that of essence of turpentine under like circumstances. When afterwards heated to near its boiling point, an active reaction sets in with considerable disengagement of heat, water is formed, and a series of hydrocarbons pass, distilling within a great range of temperatures.

An oxidised tetrahydride of naphthalene is resinedified by strong sulphuric acid in the same manner as essence of turpentine, while the pure tetrahydride dissolves in sulphuric acid without change of color. This difference offers a good test for the detection of oxidation.

has been so well studied by Messrs. Armstrong and Miller. Here, it suffices to mix the sulphonic acid, or a salt, with three or four times its weight of sulphuric acid, diluted with about one third part of water, to put a thermometer in the liquid, and to heat the retort, passing steam through the liquid, up to the point at which the hydrocarbon begins to be given off, the temperature, of course, rising with the concentration of the acid in the retort. At any desired point it is very easy to regulate the flame so as to maintain a constant temperature, and to continue the operation for several hours to insure complete decomposition at a known temperature. Under these circumstances, decomposition begins to be active at about 160° , and the temperature can be pushed to 175° or 180° without noticeable oxidation of the hydrocarbon.

We used this method to effect the separation of naphthalene and hydride of naphthalene, which is very difficult by distillation alone. The sulphonic acid of naphthalene is more readily decomposed than that of the hydride, and on heating at 160° , most of the naphthalene passes with the first portions of the distillate. The separation, however, is never complete.

We also studied a similar reaction with regard to the sulphonic acids of benzene and its homologues, and noticed, as Messrs. Armstrong and Miller have done, differences of stability of the different aromatic hydrocarbons; but in the case in which we wished particularly to apply it, viz. for the purification of pentamethylbenzene from the durols and from hexamethylbenzene, an obstacle presented itself in the difficulty of forming a sulphonic acid from the pentamethylbenzene.

It is evident there can be no question of the priority of the publication of Messrs. Armstrong and Miller, and we only desire to add to the facts which they have stated, this description of the application of their reaction to the case of the hydrides of naphthalene, which we have been studying independently for some time.

PARIS, *June 12, 1884.*

ON CASSITERITE FROM IRISH CREEK, ROCK-
BRIDGE CO., VIRGINIA.

BY W. G. BROWN.

The cassiterite at this locality is found as loose crystals and fragments, on the surface and in veins, in place.

The tin-bearing veins, which have been followed to a depth of from 12 to 20 feet, in the course of the "prospecting" which is now being carried on, occur in a coarse-grained, very much decomposed granite or gneiss, which does not contain more than a trace of tin. They run northeast to southwest conformably with the common strike of the rocks of the Blue Ridge, or in a direction nearly at right angles to this.

The cassiterite is found in the closest connection with quartz; frequently one or the other mineral, or a mixture of both, filling the fissure, with or without a definite arrangement. In some places the vein is wholly quartz, which passes into a quartz, with imbedded crystals of cassiterite; the cassiterite increasing, the quartz is sometimes enclosed as a band between two bands of cassiterite, finally the quartz is entirely replaced.

Along with the cassiterite, wolframite is found in rough crystals or irregular masses, on which an occasional crystal face is seen, mixed with the products of its disintegration, in all stages of weathering, from the almost fresh unchanged mineral to red ochre or to limonite, with only a trace of manganese. In some specimens the cassiterite is wholly imbedded in these decomposition products.

A light-colored mica, in small tables, almost invariably accompanies the cassiterite. Usually upon that portion of the vein next to the "country rock" there is a layer of this mica, or the tin-stone is banded on each side with a layer of the decomposition products of the wolframite, and then on these the mica is found. Its composition has not yet been determined.

An auriferous mispickel is found sparingly in the vein, and a hexagonal mineral which may have resulted from the alteration of beryl.

The veins of cassiterite, which are crystalline, vary in thickness from $\frac{1}{2}$ inch or less to 3 or 4 inches, with an occasional mass of

much larger dimensions. They may be solid, or may contain cavities which are lined with prismatic crystals of cassiterite up to an inch in length, and these crystals are at times covered with red ochre or with a layer of iridescent, globular limonite, or the cavities may be filled with the decomposition products of the wolframite. On breaking the apparently solid vein tin-stone the interlocking crystals often separate, sharply defined, from each other. The vein tin passes in color from brownish white through various shades of brown to reddish brown, with a dull, subresinous or adamantine lustre. Subtranslucent to opaque. It shows only traces of cleavage. Fracture even. Sp. gr. 6.536.

The crystals found thus far are comparatively dull; only very few have approached the lustre and beauty of those of Saxony and Bohemia. One of these, a compound crystal, varies from wax yellow through brown to black in color. Translucent. Resinous to adamantine lustre. Splendent. Subconchoidal to uneven fracture. Sp. gr. 6.609.

A few simple crystals are found. One a combination of the following forms, 111 (P), 110 (∞ P), 100 (∞ P ∞), 101 (P ∞). Another implanted shows the base, the combination being 111 (P), 110 (∞ P), 100 (∞ P ∞), 210 (∞ P2), 101 (P ∞); 001 (oP). On a broken crystal 110 (∞ P), 210 (∞ P2).

The angle between 111 (P), 001 (oP) was measured with a reflective goniometer, and found to be $136^{\circ} 10'$, but owing to the imperfect reflection from the faces, it was only possible to obtain this approximate result by placing small pieces of thin glass on the planes. Twinned crystals are quite common. Twinning plane 101 (P ∞). In many crystals the twinning is repeated. One compound crystal is twinned upon each of the 101 (P ∞) planes at one end, and these second crystals are again twinned, meeting from opposite angles over the centre of the principal crystal.

Most of the crystals are striated on 110 (∞ P) parallel to the edge 110 (∞ P), 100 (∞ P ∞). Besides this striation there are striations on 110 (∞ P) parallel to the edge 110 (∞ P), 101 (P ∞). These lines are very sharp and distinct, covering 110 (∞ P) with rhomboidal markings. Although at times somewhat difficult to see with the unaided eye, these striations, which are more noticeable on the dull than on the bright crystals, are more readily observed and are more characteristic than the first mentioned. They serve well as an indicator of the prism of the first order in determining compound crystals.

The cassiterite was analysed¹ by reducing at a low red heat the very finely pulverised mineral, placed in a porcelain boat in a stream of dry hydrogen. The reduction of nearly two grams was complete in about 45 minutes. The reduced mass treated with hot, strong hydrochloric acid left an insoluble residue which was ignited and weighed. This residue was treated repeatedly with hydrofluoric acid and the silica volatilised as silicon fluoride. The remaining fixed residue, which was proved to contain neither alumina, tungstic acid, nor titanitic acid, is considered tantalic acid. In the hydrochloric acid solution, which was colorless, thus showing the absence of tungstic acid, the tin was separated as stannous sulphide, and the remaining constituents separated and determined in the usual way. It may be mentioned that the tendency of the stannous sulphide to run through the filter was prevented by the addition to the wash-water of a little ammonium nitrate.

The analysis gave :

SnO ₂	94.895
SiO ₂	.760
Ta ₂ O ₅	.237
Fe ₂ O ₃	3.418
CaO	.244
MgO	.027
Ignition	.385
	<hr/>
	99.966

UNIVERSITY OF VIRGINIA, June, 1884.

Contributions from the Chemical Laboratory of Harvard College.

XLIV.—ON MUCOPHENOXYBROMIC ACID.²

BY HENRY B. HILL AND EDWARD K. STEVENS.

The products which are formed when mucobromic acid is treated with a large excess of baric hydrate, have already been de-

¹ Becke, Zeit. f. Krystal. 1878, II, S. 318, and Rammelsberg, Leit. f. d. quant. chem. Analyse, 1874, S. 68.

² Proceedings American Acad. Arts and Sciences.

scribed by O. R. Jackson and one of us.¹ Formic and dibromacrylic acids were found to be the first products of this reaction, although even in the cold a part of the dibromacrylic acid was further converted into brompropionic acid. Later experiments undertaken with the view of avoiding this secondary decomposition, showed that an entirely different reaction ensued when the conditions were so modified that the solution was at no time strongly alkaline. The chief product formed in this case was easily found to be an acid containing four atoms of carbon and one of bromine; but the determination of its constitution proved to be a matter of more difficulty, and a description of it must therefore be postponed until it can be further studied. Since it seemed possible that sodic ethylate or potassic phenylate might react upon mucobromic acid and yield similar products, whose constitution could more easily be determined, we turned our attention in this direction. Although we have been unable to obtain any such products by the action of sodic ethylate, potassic phenylate has given us well-defined products containing the phenoxyl group.

Mucophenoxybromic Acid.

Potassic phenylate acts upon potassic mucobromate in aqueous solution at ordinary temperatures; but the isolation of the potassic mucophenoxybromate thus formed is somewhat difficult, and we have not been able to obtain uniform results in our various preparations. We have found it advantageous to use a large excess of potassic phenylate, and to add also potassic hydrate in quantity sufficient to neutralise the mucobromic acid taken. We usually have dissolved 25 grams of crystallised phenol and 17.5 grams of ordinary potassic hydrate in 30 grams of water, and after the solution is well cooled, have added 20 grams of mucobromic acid. After the lapse of a short time small compact rhombic crystals of the new potassium salt begin to separate, and the reaction is ordinarily completed in less than an hour. The crystals should then be collected at once, drained by the pump, and washed with a little cold water. Hydrochloric acid added to an aqueous solution of the salt then precipitates mucophenoxybromic acid in clustered needles, which, when dried over sulphuric acid, gave the following results:

¹ This Journal **3**, 105; and Proc. Amer. Academy of Arts and Sciences **16**, 188.

I. 0.2156 gram substance gave on combustion 0.3486 gram CO_2 and 0.0525 gram H_2O .

II. 0.2250 gram substance gave 0.1564 gram AgBr.

III. 0.2168 gram substance gave 0.1504 gram AgBr.

	Calculated for $\text{C}_4\text{H}_2(\text{OC}_6\text{H}_5)\text{BrO}_3$.	I.	Found. II.	III.
C	44.28	44.11		
H	2.58	2.71		
Br	29.52		29.58	29.52

When crystallised from hot water, mucophenoxybromic acid forms small flat prisms concentrically grouped, which melt at $104-105^\circ$. The acid is readily soluble in hot water, sparingly in cold; readily soluble in alcohol or ether, soluble in hot benzol or chloroform, and almost insoluble in carbonic disulphide or ligroin. An aqueous solution of the acid reduces silver oxide on warming, and gives with ferric chloride a whitish precipitate.

Potassic Mucophenoxybromate. $\text{KC}_4\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_3$. The salt obtained by the action of potassic phenylate upon mucobromic acid was recrystallised several times from warm water. It formed then oblique tabular crystals quite soluble even in cold water. The salt is more stable in aqueous solution than the corresponding mucobromate, and yet suffers quite rapid decomposition at temperatures near 100° . The salt dried by exposure to the air contains no water of crystallisation.

I. 0.4314 gram of the salt gave on ignition with H_2SO_4 0.1227 gram K_2SO_4 .

II. 0.4430 gram of the salt gave on ignition with H_2SO_4 0.1255 gram K_2SO_4 .

	Calculated for $\text{KC}_4\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_3$.	I.	Found. II.
K	12.65	12.76	12.72

Baric Mucophenoxybromate. $\text{Ba}(\text{C}_4\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_3)_2 \cdot 3\text{H}_2\text{O}$. This salt was obtained by neutralising a cold aqueous solution of the acid with baric carbonate, and allowing the solution thus obtained to evaporate spontaneously. It separated in leafy rhombic crystals, which were very soluble in water. On warming the solution decomposition ensued. The air-dried salt contained three molecules of water, one of which it lost over sulphuric acid, the rest at 100° .

I. 0.8147 gram of the air-dried salt lost over H_2SO_4 0.0213 gram H_2O , and in addition 0.0403 gram at 100° .

II. 0.7863 gram of the air-dried salt lost over H_2SO_4 0.0201 gram H_2O , and in addition 0.0397 gram at 100° .

	Calculated for $\text{Ba}(\text{C}_4\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_3)_2 \cdot 3\text{H}_2\text{O}$.	I.	Found. II.
H_2O	2.46	2.61	2.56
$3\text{H}_2\text{O}$	7.39	7.56	7.61

0.4628 gram of the salt dried at 100° gave on ignition with H_2SO_4 0.1599 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_4\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_3)_2$.	Found.
Ba	20.23	20.32

When treated with an excess of an alkaline hydrate, mucophen-oxybromic acid, like mucobromic, is decomposed, and yields a substituted acrylic acid together with formic acid.

Phenoxybromacrylic Acid.

We have found it most convenient to dissolve equal weights of potassic hydrate and potassic mucophenoxybromate each in their own weight of water, and to mix the hot solutions. On cooling, potassic phenoxybromacrylate separates in well-formed crystals. From these, by the addition of hydrochloric acid, we prepared the acid which, when recrystallised from hot water and dried over sulphuric acid, gave the following results:

I. 0.2037 gram of the substance gave on combustion 0.3307 gram CO_2 and 0.0553 gram H_2O .

II. 0.2027 gram of the substance gave 0.1577 gram AgBr .

III. 0.2238 gram of the substance gave 0.1739 gram AgBr .

	Calculated for $\text{C}_3\text{H}_2(\text{OC}_6\text{H}_5)\text{BrO}_2$.	I.	Found. II.	III.
C	44.44	44.27		
H	2.88	3.02		
Br	32.93		33.11	33.07

Phenoxybromacrylic acid crystallises from hot water in long silky needles, which melt at 138° . It is almost insoluble in cold water, and is somewhat sparingly soluble even in boiling water. In ether or alcohol it is very soluble; in chloroform or benzol it dissolves on

warming, and crystallises as these solutions cool. Carbonic disulphide dissolves it with more difficulty.

Potassic Phenoxybromacrylate. $\text{KC}_3\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_2$. On cooling the hot solution of potassic mucophenoxybromate in potassic hydrate, potassic phenoxybromacrylate separates in well-formed rhombic plates, which may be recrystallised from hot water, although they are quite soluble even in cold water. The air-dried salt proved to be anhydrous.

I. 0.5073 gram of the air-dried salt gave on ignition with H_2SO_4 0.1588 gram K_2SO_4 .

II. 0.5077 gram of the air-dried salt gave on ignition with H_2SO_4 0.1572 gram K_2SO_4 .

	Calculated for $\text{KC}_3\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_2$.	I.	Found.	II.
K	13.91	14.06		13.90

Baric Phenoxybromacrylate. $\text{Ba}(\text{C}_3\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_2)_2 \cdot 5\text{H}_2\text{O}$. On neutralising a boiling solution of the acid with baric carbonate, and evaporating on the water-bath, the barium salt was obtained in the form of radiating prisms, which were permanent in the air and hardly lost in weight over sulphuric acid. It was freely soluble in cold water. The air-dried salt gave on analysis:

I. 1.2120 gram of the air-dried salt lost at 110° 0.1535 gram H_2O .

II. 1.0468 gram of the air-dried salt lost at 110° 0.1345 gram H_2O .

III. 0.6687 gram of the air-dried salt lost at 110° 0.0855 gram H_2O .

	Calculated for $\text{Ba}(\text{C}_3\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_2)_2 \cdot 5\text{H}_2\text{O}$.	I.	Found.	III.
H_2O	12.66	12.67	12.85	12.78

0.5017 gram of the salt dried at 110° gave on ignition with H_2SO_4 0.1873 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_3\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_2)_2$.	Found.
Ba	22.06	21.95

Calcic Phenoxybromacrylate. $\text{Ca}(\text{C}_3\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_2)_2 \cdot 5\text{H}_2\text{O}$. The calcium salt was prepared from the acid by neutralising its aqueous solution with calcic carbonate. It was readily soluble in water, and crystallised on cooling its concentrated solution in clustered needles, which were permanent in the air or over sulphuric acid.

I. 0.9361 gram of the air-dried salt lost at 100–105° 0.1381 gram H₂O.

II. 0.7563 gram of the air-dried salt lost at 100–105° 0.1122 gram H₂O.

	Calculated for Ca(C ₃ H(OC ₆ H ₅)BrO ₂) ₂ ·5H ₂ O.	I.	Found.
H ₂ O	14.66	14.75	14.84

0.5046 gram of the salt dried at 100–105° gave on ignition with H₂SO₄ 0.1310 gram CaSO₄.

	Calculated for Ca/C ₃ H(OC ₆ H ₅)BrO ₂) ₂ .	Found.
Ca	7.64	7.64

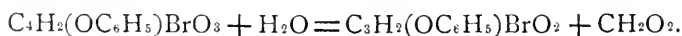
Argentich Phenoxylbromacrylate. AgC₃H(OC₆H₅)BrO₂. The silver salt may be precipitated by the addition of argentic nitrate to a hot aqueous solution of the acid. It crystallises in needles which may be recrystallised without decomposition from boiling water. When dried over sulphuric acid, the salt gave the following results:

I. 0.4464 gram of the salt gave on precipitation with HBr 0.2391 gram AgBr.

II. 0.4240 gram of the salt gave on precipitation with HBr 0.2268 gram AgBr.

	Calculated for AgC ₃ H(OC ₆ H ₅)BrO ₂ .	I.	Found.
Ag	30.85	30.77	30.72

Phenoxylbromacrylic acid is therefore one of the products formed from mucophenoxylbromic acid by the action of potassic hydrate. The mother liquors from which the potassic phenoxylbromacrylate had crystallised yielded on acidification with dilute sulphuric acid and distillation an acid distillate, which gave with ferric chloride and bromine water reactions showing the presence of small quantities of phenol. When neutralised with calcic carbonate and evaporated, it left calcic formiate, which was identified by its characteristic behavior with argentic nitrate and mercuric chloride. The decomposition of mucophenoxylbromic acid by potassic hydrate may therefore be expressed by the reaction:



While dibromacrylic acid passes readily into brompropionic and malonic acids in an alkaline solution, phenoxylbromacrylic acid is apparently unaltered by aqueous potassic hydrate. Even after

long boiling in a concentrated solution (2 : 1) no potassic bromide is formed.

Phenoxybrommaleic Acid.

On warming a solution of mucophenoxybromic acid with argentic oxide, metallic silver is readily formed. If the solution is then heated to boiling, and the silver precipitated by hydrochloric acid, the filtered solution deposits on cooling phenoxybrommaleic acid in the form of fine felted needles. Their melting point, when taken in the ordinary way, we found to be 103-104°; but when slowly heated, the melting point was materially lowered, probably through the formation of the anhydride. From the analysis of substance which had been dried over sulphuric acid, it would seem that here also a certain amount of the anhydride was formed, and that in this respect its behavior is perfectly analogous to that of dibrommaleic acid which is partially converted into anhydride by drying, as one of us has shown:¹

I. 0.1213 gram of substance dried over H₂SO₄ gave on combustion 0.1935 gram CO₂ and 0.0245 gram H₂O.

II. 0.2204 gram of substance dried over H₂SO₄ gave 0.1494 gram AgBr.

	Calculated for C ₄ H ₂ (OC ₆ H ₅)BrO ₄ .	Calculated for C ₄ (O ₂ C ₆ H ₅)BrO ₃ .	I.	Found.	II.
C	41.81	44.61	43.51		
H	2.44	1.86	2.25		
Br	27.87	29.74			28.85

Ratio of carbon to bromine atoms as found = 10 : 0.995.

Argentic Phenoxybrommaleate. Ag₂C₄(OC₆H₅)BrO₄. By the addition of argentic nitrate to an aqueous solution of the acid, the silver salt is precipitated in the form of clustered rhombic plates, which may be recrystallised from boiling water without decomposition. The dry salt is decomposed suddenly by heat, but without detonation.

I. 0.3922 gram of the salt dried over H₂SO₄ gave on precipitation with HBr 0.2928 gram AgBr.

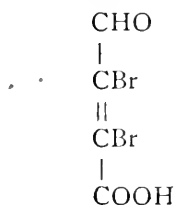
II. 0.2903 gram of the salt dried over H₂SO₄ gave on precipitation with HBr 0.2168 gram AgBr.

	Calculated for Ag ₂ C ₄ (OC ₆ H ₅)BrO ₄ .	I.	Found.	II.
Ag	43.12	42.88		42.90

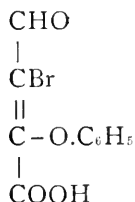
¹ This Journal 3, 98; and Proceedings American Acad. of Arts and Sciences 16, 178.

The relation which mucophenoxybromic acid bears to mucobromic is sufficiently shown by its conversion into phenoxybromacrylic and phenoxybrommaleic acids under conditions identical with those necessary to the formation of dibromacrylic and dibrommaleic acids from mucobromic. Furthermore, it is evident that the extreme stability of the phenoxybromacrylic acid in alkaline solution shows that the phenoxyl group has taken the place of the bromine atom which is so readily removed from the corresponding dibromacrylic acid in the formation of brompropionic acid.

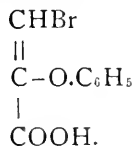
If mucobromic acid be written,



it follows that mucophenoxybromic acid has the form,



and the acrylic acid derived from it has the form,



REVIEWS AND REPORTS.

REPORT ON PROGRESS IN PHYSIOLOGICAL CHEMISTRY.

Liver, Bile, and Glycogen.

Facts acquired during the last few years concerning anatomical changes in the cells of the salivary, gastric and pancreatic glands in periods of *rest* and *activity*, and the connection of these changes with changes in chemical composition, have led several investigators to study the minute structure of the liver cells under like conditions, to trace, if possible, any connection here between structural differences and the secretion of bile or the formation of glycogen. Langley¹ has recently published a preliminary account of his results in the study of this question. The *resting* liver cells of the frog, toad, newt, pigeon and various mammals have certain common points of structure; the protoplasm is arranged in the form of a network, the meshes of which are nearly of the same size throughout the entire cell. Within the protoplasmic network is an interfibrillar substance, consisting of spherical granules, probably proteid in their nature, spherical globules of fat, and a hyaline substance filling up the spaces not occupied by the two former and consisting partly of glycogen and probably also of a proteid body. These spherical proteid granules described by Langley as present all through the resting cells have apparently been overlooked by previous investigators, even by Klein² and Kupffer. Apparently the best method for bringing out the granules and also the fat globules is to place a portion of liver in 1 per cent. osmic acid for 24 hours, then in alcohol for several days, after which sections can be cut. Sections thus prepared show the globules and granules imbedded in a homogeneous cell substance. Placed in iodine solution for a few minutes, portions of the interfibrillar substance of the cell take on a reddish-brown color, due to the presence of glycogen. The liver of a hungry frog, as in summer time, shows granules scattered equally throughout the cell with almost an entire absence of glycogen. During the long winter fast the cells undergo a decided change in appearance, the granules being more confined to the inner portion of the cell, forming a marked inner granular zone. At the same time the glycogen increases in amount, being stored up in the clear outer zone. The two zones are very clearly outlined in an osmic acid and iodine preparation.

¹ Proceedings of the Royal Society **34**, 20.² Quart. Journ. Med. Soc. n. s. **19**, 161.

As has been previously ascertained, the changes which take place during fasting in the cells of some of the gastric glands are very similar to the changes occurring during digestion. Likewise Langley has found in the liver of the frog that the changes which take place when the animal is fed are in nearly every respect like those which are gradually established during the winter fasting. The extent of the change, however, is dependent upon the state of the liver cells before the animal is fed, the change being much more marked when the cells start with a small outer non-granular zone. In such a case the outer zone becomes quite large by the 6th to 8th hour of digestion, while at the end of the 24th to 30th hour the cells become granular throughout. Langley observed that while a decrease of granules goes hand-in-hand with an increase of glycogen and an increase of granules with a decrease of glycogen, still a certain amount of variation may take place without any corresponding variation in the other, and thus Langley is led to the view that the formation of granules and the formation of glycogen are independent processes. But from analogy it seems fair to presume that the granules of the hepatic cells are destined to give rise to some one or more constituents of the bile, and Langley suggests that by proper chemical treatment these granules may be made to yield some portion of the bile salts.

In the study of the mammalian liver, Langley confined himself almost exclusively to the mole, with results similar to those mentioned in the case of the amphibian livers. In cells in which the digestive changes are less advanced, the glycogen may only partially surround the nucleus or may be accumulated more or less to one side of the nucleus. In no case did Langley observe the lumps or granules of glycogen observed by Kayser. Bock and Hofmann¹ experimented on rabbits, and found the glycogen accumulated in amorphous form around the nucleus. Langley's observations accord with theirs in this respect, although the former observer considers that the glycogen is stored up in the spaces of a protoplasmic network.

Quite independent of Langley, Afanassiew² has likewise studied the anatomical alterations of liver during different conditions of activity. Afanassiew's experiments were made mostly on dogs, the following general plan being adopted: First, the livers of animals deprived of food for a period of from one to three days were compared anatomically, with the livers of animals fed on a mixed or flesh diet, at the same time the amount of glycogen in the liver was determined in both cases. Very soon after the commencement of the experiment, a great difference was noticed in the structure of the liver, particularly in the cell elements and also in the quantity of glycogen, whereupon Afanassiew attempted to separate as far as possible the formation of bile from the formation of glycogen. For this purpose in the first series of experiments

¹ Virchow's Archives 56, 201.

² Pflüger's Archiv 30, 385.

dogs were employed which had been fed purely on a carbohydrate diet, while in the other series the animals experimented on were fed on a purely flesh diet, meat or pure blood fibrin. The liver in each was examined quantitatively for glycogen. In still another series of experiments the secretion of bile was increased above the normal, without the use of food. This was accomplished by cutting the liver nerves of a curarized animal and then injecting pilocarpin into the blood, which materially increases the flow of bile.

Afanassiew noticed, conformable with the observations of Langley, that the liver cells of an animal fed on fibrin showed in general the characters of the liver cells of a hungry animal. As these cells are not colored brownish-red by iodine, and as the addition of osmic acid does not increase the granulations within the cell, Afanassiew concludes that by feeding with fibrin, the content of finely granular albuminous matter in the liver cell is increased. After feeding with potatoes and sugar, whereby the liver becomes exceedingly rich in glycogen, the liver cells appear very large, filled to excess with coarse granules or indistinct amorphous particles or spots of glycogen, with the protoplasmic network ordinarily not perceptible. The small sharply outlined granules which are so noticeable in the hungry condition, or after feeding flesh, are hardly ever to be seen. Again, if the formation of bile be increased by cutting the liver nerves, or by feeding with albuminoid food, the cells become correspondingly large, and contain between their protoplasmic threads, large numbers of fine, sharply outlined granules, which in chemical nature approach albuminoid matter. This fact explains the resistance of such cells to potassium hydroxide. When, on the other hand, the cells become relatively poor in albuminous matter, as during increased formation of glycogen, then the cells rapidly decompose in concentrated solutions of potassium hydroxide.

In a fat diet, fat globules are noticeable in the cell, and after taking mixed food, appearances due to a combination of all of the former are noticed. When a healthy animal is allowed to become hungry, the liver loses first the glycogen, then in part the water; the albumin remains the longest, although a portion of this is decomposed with formation of fat. There appears to be no division of cells with a difference in function, but all of the cells of the liver lobe form both bile and glycogen.

If an increased secretion of bile depends upon an increased circulation of blood, it would follow that a great accumulation of glycogen must diminish the secretion of bile, and Spiro¹ indeed found that the addition of carbohydrates to a flesh diet retarded the increase of bile secretion during digestion. As a result of experiments with toluylene-diamine Afanassiew found that the formation of bile is increased by an excessive decomposition of the red blood

¹ Du Bois Reymond. *Archiv f. Physiol. Supplement Band*, 1880.

corpuscles, from which it would appear that under normal circumstances the decomposition of the red blood corpuscles, within certain physiological limits, may give a stimulation to the secretion of bile.

Formation of bile coloring matter.—Tarchanoff¹ found, after injecting a solution of haemoglobin into the blood of a dog with a biliary fistula, a decided increase of coloring matter in the freshly secreted bile. This fact he considered as a support to the view of a conversion of the blood coloring matter into bilirubin outside of the liver. Stadelmann,² after calling attention to Tarchanoff's experiments, has given the results of his study of the question. The method employed in determining the coloring matter was based upon the use of the spectroscope according to the method of Vierordt.³ In using this method, however, the bile must be examined as fresh as possible, since on standing exposed to air it acquires a green color, owing to the conversion of bilirubin into biliverdin by oxidation, and as the latter has far greater absorbing power, a higher percentage of coloring matter is obtained. Thus Stadelmann found that the coloring matter of a specimen of bile, after standing two days, increased from .074 per cent. to .110 per cent.

A large dog with a biliary fistula and fed upon a constant diet yielded in 12 hours, as a mean of 13 estimations, 147.5 cc. of bile with .082 gram of bilirubin = .0577 per cent. After injecting 20 grams of moist haemoglobin dissolved in 100 cc. of water into the jugular vein, a strongly bloody urine was passed, without however any icterus of the skin. Two hours after the injection a decided increase of the absolute quantity of bile coloring matter was noticed, while at the same time the quantity of bile was diminished. This was followed after 12 hours by an increase of the secretion of bile with a sinking of the relative content of the coloring matter. As compared with the normal average figure, the secretion of coloring matter in the first 12 hours showed an increase of .024, while in the second 12 hours an increase of .042 was noted. This would seem to indicate that the liver itself must first form bilirubin from the absorbed haemoglobin, and that Tarchanoff's view of the conversion of the haemoglobin into bilirubin in the blood itself is probably incorrect; for while bilirubin, as Vossius⁴ has found, appears in the bile directly after its injection, and is secreted after 5 or 6 hours, an injection of haemoglobin solution does not produce an increased secretion of bile coloring matter until 3-4 hours after its injection, but on the other hand the secretion continues for 20-24 hours.

Stadelmann has likewise found that injection of .6-.8 per cent. sodium chloride solution produces in a similar manner a not inconsiderable increase of the absolute bilirubin secretion, there being

¹ Jahresbericht für Thierchemie 4, 305.

² Archiv f. exper. Pathol. u. Pharm. 15, 237.

³ Die Anwendung des Spectralapparates. Tübingen, 1873.

⁴ Jahresbericht für Thierchemie 9, 246.

at the same time a considerable diminution of the bile secretion. The bile itself becomes turbid and very noticeably green in color. This abnormal feature of the secretion Stadelmann considers due to an irritation of the hepatic cells or of the nerve endings in the liver caused by the abnormal condition of the blood.

Influence of food upon the composition of the bile.—It has usually been supposed that the composition of bile, or more strictly speaking the proportion of glycocholic to taurocholic acid, was a more or less constant one. Hüfner,¹ however, has found a decided variation in the amount of these acids contained in ox bile; thus, as a result of a large number of examinations, samples were obtained in which the two acids were present in approximately the same quantities, others in which the amount of glycocholic acid was fully five times larger than the amount of taurocholic acid. In the latter case the bile gave Hüfner's reaction with hydrochloric acid and ether quite easily; when, however, the taurocholic acid was in excess or even equal to the glycocholic acid, the crystallisation was not obtained. Emich² has found this non-crystallisation to be due apparently to the solvent action of the non-crystallisable taurocholic acid on the glycocholic. Hüfner has supposed this variation in composition due to the food. Carl v. Voit³ has found, however, that this is not the case with dog's bile. Taking the determination of sulphur as an index of the amount of taurocholic acid, the following results were obtained:

Animal.	Food Stuff.	Per cent. of Sulphur in dried Bile.	Per cent. of Sulphur in crystallised Bile.
Dog No. 3.	Flesh	2.24	4.52
" "	"	2.33	4.01
" "	Potatoes	1.90	4.25
" "	Gelatin	2.33	4.50
" "	Fat	3.14	4.61
" "	Potatoes	2.63	4.26
" " 4.	Flesh	2.68	4.47

According to Strecker and Hoppe-Seyler, dog's bile contains only taurocholic acid. These two investigators, likewise Bensch, as well as Bidder and Schmidt, found the amount of sulphur to correspond to about 6 per cent. Kunkel and Spiro, however, obtained results similar to the above.

By drawing away the bile, v. Voit finds that the amount of unoxidised sulphur in the urine is greatly diminished, which is in close agreement with the previously obtained results of Kunkel.⁴ In normal animals the relation of unoxidised sulphur to sulphuric acid in a flesh diet is as 1:1.2, in a gelatin diet 1:5.5. In the case of a dog with a biliary fistula the relation in a flesh diet is 1:2.7, in a gelatin diet 1:6.2. Taurine is the main source of the unoxidised sulphur in the urine, though not the only one.

¹Journal für prakt. Chemie 25, 97.

³Jahresbericht für Thierchemie 12, 417 et seq.

²Monatshefte für Chemie 3, 330.

⁴Jahresbericht für Thierchemie 6, 192.

According to all previous observers, the taking of food causes an increase in the secretion of bile. Hitherto, however, there has been a great divergence in the results obtained, due primarily to the lack of precision in arranging the diet and collecting the bile. As the amount of water in bile is exceedingly variable, the content of solid matter is the only certain indicator of the progress of the secretion. In hunger the secretion is not quite regular. The variations apparently depend on the irregular outflow of the then highly concentrated glairy bile. At night the secretion is diminished, due probably to the smaller decomposition of fat. After eating meat in large quantities, as for example 1266 grams meat and 398 grams of water, the maximum secretion takes place, 0.98 gram dry bile in the first hour, followed by a gradual sinking to 0.45 gram. The following table gives a few of the important results obtained by v. Voit, the figures giving the entire quantity of bile in grams secreted during the 24 hours, together with the amount of food taken.

DOG NO. 3.					
	Food.				
				Fresh.	Dry.
Hunger	.	.	.	124.3	8.46
"	.	.	.	78.8	7.26
750 flesh	.	.	.	272.4	12.16
1345 "	.	.	.	323.9	13.80
100 fat	.	.	.	173.7	7.43
1500 flesh and 130 fat	.	.	.	272.4	11.14
225 starch	.	.	.	132.0	8.81
545 bread	.	.	.	240.0	9.80
1764 potatoes	.	.	.	212.3	9.45
120 gelatin	.	.	.	150.5	7.37
150 "	.	.	.	202.7	10.76
1500 flesh and 76 gelatin	.	.	.	347.7	13.13

Thus in hunger only $\frac{1}{2}$ to $\frac{1}{3}$ of the usual quantity of bile is secreted. In the latter days of the hunger period, much less bile is secreted than in the first. Increased additions of albumin cause an increase of bile, though not a proportional one.

Bile perhaps originates only from the albumin, certainly it must in those cases where only albumin is decomposed. At the same time gelatin, carbohydrate and fat do not alter materially the quantity of bile, but as they spare the albumin they can thus indirectly aid the formation of bile.

Spiro considers the increase in the formation of bile after eating as due essentially to the decomposition in the liver of the absorbed organic matter. Voit, however, cannot accept this view, since the greatest increase of bile is noticeable during the first hour or so, at which time only a small portion of the food taken could be absorbed. It is more probably dependent on reflex action, or more probably still on the washing out of the thick, glairy bile of the hungry and night hours from the bile ducts and capillaries

by the water so abundantly absorbed. All observers have noticed the decided influence of water upon the secretion of bile.

Action of bile acids on proteid matter, etc.—It has long been an interesting question as to the probable action of the bile salts in the intestinal canal. Since the acids of the chyme are stronger than the bile acids, it follows that the latter will naturally be liberated by the former. The only thing in the bile itself which can act as a neutralising agent is a small quantity of acid sodium carbonate. When, however, the contents of the intestines react acid, free bile acids must be present. Lehmann long ago¹ recognised this fact, and various investigators² since then have demonstrated that the contents of the intestines, even to their entire length, ordinarily show an acid reaction, although the mucous membrane itself generally has an alkaline reaction. It is thus evident that in the intestines, as a rule, free bile acids are to be found, and not their neutral salts. Thus Maly and Emich,³ in order to understand the behavior of the bile in the intestines, have made a special study of the behavior of the free bile acids towards the three albuminous bodies, egg-albumin, propeptone and peptone. The action of the pure bile acids on the above substances has never been investigated, although Brücke, Schiff, Hammarsten and Moleschott have placed on record the results of their study of the so-called duodenal precipitate which is readily obtained when bile is added to the acid chyme or to an artificial pepsin digestion.

Maly finds that a one per cent. solution of taurocholic acid added to a one per cent. solution of peptone or propeptone produces an immediate white milky precipitate or turbidity difficult of filtration, which is easily soluble in dilute sodium carbonate, but reprecipitated by acetic or hydrochloric acid. The precipitate is very readily soluble also in solutions of soap, sodium glycocholate and taurocholate, even also in the slightly alkaline blood-serum. The precipitate formed as above is apparently not a compound of the peptone or propeptone with taurocholic acid, but a modified form of taurocholic acid itself. In fact, a solution of sodium chloride added to taurocholic acid produces the same effect as a solution of peptone. Peptone and propeptone appear to combine with taurocholic acid, but the compound is even more soluble than either of the two.

Cold saturated solutions of glycocholic acid are not precipitated by peptone solution. If, however, a solution of sodium glycocholate, peptone or propeptone and some hydrochloric acid are mixed together, a precipitate is obtained, which, however, contains but little if any peptone, mainly glycocholic acid.

Addition of taurocholic acid to a solution of egg-albumin produces an immediate, heavy flocculent precipitate, easily filtered,

¹ Lehrbuch d. physiolog. Chem. 2, 69.

² Schmidt-Mulheim, Jahresbericht für Thierchemie 9, 210. Uffelmann, *ibid.* 11, 305. Nothnagel, *ibid.* 11, 309.

³ Monatshefte für Chemie 4, 89, 1883.

which is readily soluble in all alkaline fluids, but is insoluble in alcohol, and contains both albumin and taurocholic acid. The latter however can be, in part at least, extracted by boiling with alcohol. Maly's experiments further show that the albumin is completely precipitated, more so even than when coagulated by heat, and that with proper precautions the method can be advantageously employed for quantitative purposes. Presence of large quantities of sodium chloride hinders the precipitation. Quantitative experiments also showed that taurocholic acid is an excellent agent for separating coagulable albumin from peptone or propeptone, the latter not being precipitated, while the former is completely so.

Glycocholic acid does not precipitate albumin. Thus these reactions, which may be assumed to take place in the intestinal canal, may serve to separate the coagulable albumin, rendering the peptones more readily absorbable, but whether the taurocholic acid precipitate is readily digestible is a question not yet answered.

Emich¹ has made a study of the antiseptic action of the bile acids and their behavior towards both the formed and unformed ferments. It has for a long time been considered that bile possesses antiseptic properties, although hitherto no experiments have been tried to verify this assumption. Emich has found that the presence of one per cent. of taurocholic acid in a solution or mixture will prevent the growth of bacteria in flesh and pancreas extracts, and that both lactic and alcoholic fermentation is hindered by its presence. Glycocholic acid in most cases acts in a similar manner, although not so energetically.

Brücke, Hammarsten and others have long ago demonstrated that the addition of a small quantity of bile to a pepsin digestion would completely suspend its activity. Emich has found that the presence of .2 per cent. taurocholic acid hinders the solvent action of gastric juice, while glycocholic acid is entirely without influence even when present to the extent of 1 per cent. In a similar manner the diastatic action of saliva and pancreatic juice is hindered by the presence of .2 per cent. taurocholic acid, and to a less extent by glycocholic acid.

R. H. CHITTENDEN.

(To be continued.)

THOMSEN'S "THERMOCHEMICAL RESEARCHES."

In the second volume of this work we find determinations of the most important combinations of the metalloids among themselves, including, therefore, many of the most valuable fundamental data of the science. A portion of this matter has appeared before, but is here revised and enlarged, while much is new, including the

¹ Monatshefte für Chemie 4, 108, 1883.

study of the hydrocarbons and of carbontetrachloride and perchlorethylene, the latter amongst the most difficult thermochemical investigations yet accomplished. Perhaps as interesting a point as any that Thomsen has brought out relates to the formation heat of the hydrocarbons. In Vol. II he treats of only a few typical substances, viz. methane, ethane, ethylene, acetylene and benzene, the rest being reserved for Vol. IV; but he offers a formula for the calculation of the formation heat of hydrocarbons in general, knowing their structural formulae. The substance of this chapter appeared in the "*Berichte der deutschen chemischen Gesellschaft*," 13, pp. 1321-1324, and was reviewed in this Journal, vol. II, p. 347; but as the author in his second volume presents the subject in somewhat different form and with numbers revised, it will bear another brief review in this connection.

The method of calculation is based upon the following assumptions:

1. That heat is absorbed in the gasification of carbon, and that its amount is equal to the difference between the formation heat and combustion heat of carbon monoxide.

2. That the combination heat of the atoms of gaseous carbon with each other depends upon whether there is single, double or triple union.

3. That the combination of hydrogen and gaseous carbon is exothermic, and that all the hydrogen atoms of a molecule have the same influence upon its formation heat.

Now the formation of a hydrocarbon from amorphous carbon and hydrogen at 18° C., constant pressure, may be resolved into the following steps:

1. Gasification of amorphous carbon. Let the amount of heat required for this be represented by d for each atom.

2. Combination of carbon atoms with each other. Let the amount of heat evolved by this be represented by v_1, v_2, v_3 , according as there is single, double or triple union.

3. The combination of hydrogen with the carbon nucleus. Let this combination heat be represented by r for each hydrogen atom.

4. Finally, the contraction to unit-volume (H_2); since the quantities are measured at constant pressure, an amount of heat q must be added for each volume (H_2) lost.

Hence, in general, the formation heat, H , at constant pressure, of a hydrocarbon, C_nH_{2m} , equals

$$-nd + 2mr + \Sigma v + (m-1)q.$$

For the hydrocarbons in question, adopting the usual formulae and determining experimentally the combination heat, we have:

- (1) $CH_4 = -d + 4r + q = 21750 \text{ cal.}$
- (2) $C_2H_6 = -2d + 6r + v_1 + 2q = 28560$
- (3) $C_2H_4 = -2d + 4r + v_2 + q = 2710$
- (4) $C_2H_2 = -2d + 2r + v_3 = 48170$
- (5) $C_6H_6 = -6d + 6r + 9v_1 + 2q = 1110$

The formula for benzene used is based upon the supposition that there are nine single unions in the carbon nucleus.

As stated above, d equals the difference between the formation heat and combustion heat of CO, calculated for constant volume. This is given by Thomsen as 38380 cal.; also the value of q , calculated for 18° C., as 580 cal. From the equations 1, 2, 3, 4 and 5, the value of r , v_1 , v_2 , and v_3 may be calculated. These are given by the author as follows:

$$\begin{aligned} r &= 14830, \\ v_1 &= 15350, \\ v_2 &= 14130, \\ v_3 &= -1080. \end{aligned}$$

He calls them the dynamic constants of carbon, and to them is added the combination heat of one atom of oxygen with the carbon nucleus, assumed to be the same as the combustion heat of CO, hence equal to 67670 cal. (constant volume).

The assumptions upon which this calculation is based seem somewhat hazardous; yet when the above values are used to calculate the formation heat in the five examples under consideration the accordance is extraordinary.

The following table shows the calculated results compared with the experimental.

	Formation Heat.		Combustion Heat.	
	Cal.	Exp.	Cal.	Exp.
Methane	21520	21750	212160	211930 cal.
Ethane	28730	28560	370270	370440
Ethylene	-2730	-2710	333370	333350
Acetylene	-48180	-48170	310460	310450
Benzene	-1990	-1110	788830	787950

The calculated formation heat of benzene, assuming three single and three double unions, is -51700 cal., and combustion heat 838540. Thomsen carries the subject no further, except to refer to Vol. IV for the application of the formula and constants to a large number of compounds. If the result of so doing should justify the assumptions upon which the formula is based, it will be of the highest interest. Meanwhile there are some considerations which may well be borne in mind. In the first place these formation heats are determined only indirectly as the difference between the heat of combustion of the substance and of its constituent carbon and hydrogen in the elementary state. This difference is generally small compared with the combustion heat, and an error in the determination of the latter is increased many fold in the calculation of the formation heat. Take benzene for example; there is a difference of only 0.1 per cent. between the observed combustion heat and the value calculated from Thomsen's formula, whereas in the corresponding formation heat this difference becomes 79 per cent.

There is discrepancy too in the determinations of different observers. Thomsen himself, in the publication above referred to, gives for the formation heat of benzene -18960 cal., while Berthelot and Ogier give $+5800$; and for acetylene Berthelot gives -55100 , for ethylene -9400 cal.

The following table shows the results obtained by applying Thomsen's formula to a few additional substances whose combustion heats have been determined experimentally :

	Cal.	Exp.
Propane, $\text{CH}_3-\text{CH}_2-\text{CH}_3$,	35940	30820 (Thom.)
Propylene, $\text{CH}_3-\text{CH}=\text{CH}_2$,	4480	760 (Thom.)
Allylene, $\text{CH}_3-\text{C}\equiv\text{CH}$,	-40971	-37500 (Berth.)
Dipropargyle, $\text{CH}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{CH}$,	-96250	-96390 (Thom.)
Diallyle, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$,	-5350	$+22700$ (Berth.)
Aldehyde, $\text{C}_2\text{H}_3\text{OH}$,	$+66450$	$+56500$ (Berth.)

It would seem that in order to extend satisfactorily the application of his formula, Thomsen must be able to modify very considerably the constitutional formulae or the values for combustion heat already on record.

We find in an appendix to Vol. II a chapter on oxidising and reducing agents, and one on the constitution of certain substances, SiO_2 and HFl , in water solution. This latter, together with several chapters in Vol. III (which has appeared since this review was commenced), is of special interest, as affording instances of the application of thermochemical methods to the solution of important problems to which other methods hardly reach. We purpose to note briefly some of the author's conclusions in this direction. As to SiO_2 and HFl , the thermal phenomena seem to indicate that SiO_2 has no definite neutralisation point, at least for NaOH , water probably tending to decompose the silicate; that $\text{Si}(\text{OH})_4$ is the correct molecular formula for the acid in water solution; that toward $\text{Si}(\text{OH})_4$, HFl acts as a monobasic, diatomic acid of formula HFl_2H , the normal compound result from their action being $\text{Si}(\text{Fl}_2\text{H})_4$.

As to HCl , the indication is that the true molecular formula for the acid in solution is $\text{HCl}, \text{H}_2\text{O}$ or H_2ClOH , being monobasic. The author cites facts of isomorphism, molecular volume, and specific heat in further support of this view.

For iodic acid in solution the formula is $\text{I}_2\text{O}_6\text{H}_2$.

Continuing this line of investigation, we find a chapter in Vol. III on the dilution heat of certain acid, alkaline and saline solutions, published here for the first time. Sulphuric, nitric, phosphoric, acetic and formic acids are investigated, and no indication found of the existence in solution of definite secondary hydrates, not even of the crystallisable $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$; the dilution heat being in general a continuous (hyperbolic) function of the amount of water used.

With regard to HCl , HBr , and HI there is found no indication of hydrate containing more than 2.2 or 2.8 molecules of H_2O to one molecule of acid, that being the composition of the most concen-

trated solution used; but there is evidence of the existence in concentrated solution of a hydrate containing one molecule of water; the formation heat of this hydrate is probably small, which accords with its instability. On the other hand, the author finds no evidence of a secondary hydrate in the case of the alkalis K, Na, NH_3 , at least none containing more than three molecules of water.

Taking up next saline solutions, the author proposes two questions for investigation: first, whether dilution may cause a partial decomposition of the salt, and second, whether definite secondary saline hydrates exist in solution. With but 6 exceptions out of the 35 salts studied the following law is found to hold, viz. that those salts whose dilution heat is positive, dissolve when in anhydrous condition with evolution of heat; and those whose dilution heat is negative, dissolve with heat absorption. Now from his study of solution heats the author was led to conclude that those anhydrous salts and chlorine, bromine and iodine compounds which dissolve in water with heat evolution, form also crystallisable compounds with water (or are completely decomposed); and that those salts and chlorine, bromine and iodine compounds which form no crystallisable compounds with water (and are not fully decomposed) dissolve with heat absorption. And the author is therefore disposed to conclude that those substances which have a positive dilution heat form crystallisable combinations with water, while those whose dilution heat is negative form no crystallisable combination with water.

The next conclusion is that those salts which dissolve with heat evolution and crystallise with water also exist combined with water in solution; but that there is no indication of the existence of different saline hydrates in solution dependent on the quantity of water present; and that the dilution heat of acid, alkaline, and saline solution which is a function of the latter quantity is allied in cause to the heat disturbance which takes place on mixing liquids, such as alcohol with water, ether, chloroform, bisulphide of carbon, &c., which do not act chemically upon each other; and that the common cause is a transfer of energy between groups of different molecules, by which results an equilibrium which is not normal to the substance at the initial temperature, and hence produces an absorption or liberation of heat.

Upon these points Berthelot is not in accord with Thomsen. The former finds evidence in both the thermal and chemical phenomena of the existence of secondary hydrates, and makes them, as well as the partial decomposition of certain salts by water, play an important role in chemical statics.

Another chapter is upon a somewhat related subject, viz. the constitution of hydrated salts. In this are given the heats of combination of the anhydrous salt and its water of crystallisation, molecule by molecule; and the curious fact is brought out that in very many cases the latter taken in pairs have the same combination heat. The author suggests that this may be indicative of the symmetri-

cal relation of the water in the molecule of the hydrated salt, or, more probably, that the molecular weight of liquid water is double that of its vapor.

Another chapter is given to the determination of a large number of solution heats, and the remainder of the volume, with the exception of a special chapter on the energy and electro-motive force of galvanic combinations, is devoted to the principal combinations of the metals.

A. V. E. YOUNG.

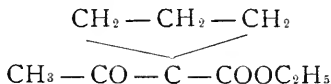
NOTES.

On Trimethylene Derivatives.

By treating sodium ethyl aceto-acetate and other compounds of a similar character with bromine addition products of certain members of the unsaturated series of hydrocarbons, W. H. PERKIN, Jr., has succeeded in producing a number of interesting compounds which are derivatives of a body consisting of a closed chain of three or four carbon atoms.

The general method of formation involved in the production of these substances becomes evident by a consideration of the first one prepared, *i. e.* that obtained by the action of trimethylene bromide upon sodium ethyl aceto-acetate.

To a solution of sodium in absolute alcohol, ethyl aceto-acetate and trimethylene bromide were added in proper proportions, and the mixture heated for a time on the water bath. This resulted in the production of a substance to which the following formula was given:

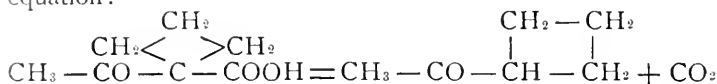


The correctness of the empirical formula was proved by satisfactory analyses and by a vapor density determination. To this substance the name ethyl aceto-tetramethylene carbonate was given.

The acid corresponding to this ether was obtained by treatment with sodium ethylate and subsequent acidifying with sulphuric acid; it was obtained without difficulty in crystalline form. The formula was substantiated by analysis of the acid itself and of the silver salt. In order to be sure that this acid was the result of nothing more than simple saponification of the ether, the silver salt was treated with ethyl iodide, and, as indicated by the boiling point, the ether was thus reproduced.

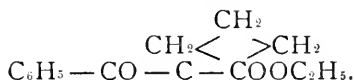
The next transformation effected was the removal of carbon dioxide from the acid. This was accomplished by simple dry distillation by heating the acid on an oil bath to 180° C. Carbon dioxide was actively given off and a light volatile oil was distilled.

The transformation thus effected is represented in the following equation:

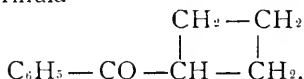


To this compound the name acetyl tetramethylene is given.

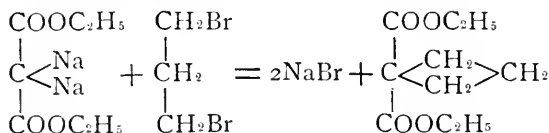
By treating sodium ethyl benzoyl-acetate with trimethylene bromide, by a process similar to the one already described in connection with the ether first considered, ethyl benzoyl-tetramethylene carbonate was produced. The formula of this substance is analogous to that of the corresponding acetyl compound, *i. e.*



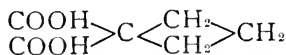
From this ether by saponification the acid was obtained, and from the latter by dry distillation the compound benzoyl-tetramethylene of the formula



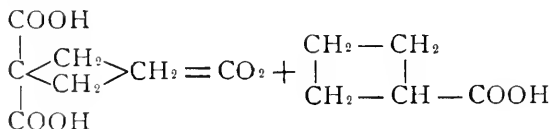
The compounds of special interest next produced are the mono- and dicarbonic acids of tetramethylene, which were obtained by starting with trimethylene bromide and sodium ethyl-malonate. The reaction taking place first was the following:



Saponification of this ether produced the dicarbonic acid of tetramethylene, *i. e.*

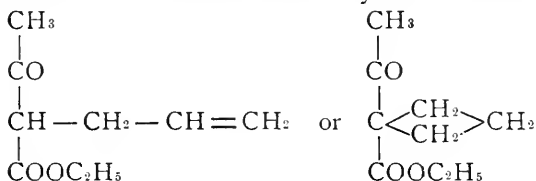


The monocarbonic acid was obtained from the dicarbonic acid by dry distillation thus:



Analyses of these acids, and of their salts, gave figures in accordance with the formula given.

Now let us consider the evidence upon which are based the structural formulæ of the compounds thus far considered, particularly with regard to the presence in them of this closed chain of carbon atoms known as the tetramethylene group. Referring in the first place to ethyl aceto-tetramethylene-carbonate, it is evident at first that one of two formulæ may be ascribed to it, either



The first corresponds to ethyl-allylaceto-acetate, the second contains a ring formed of four carbon atoms. The properties of the ether under consideration are, however, entirely different from those of ethyl allyl-aceto acetate, and therefore the second formula must be accepted as the correct one. The following general statements, applying to all the compounds discussed, are made:

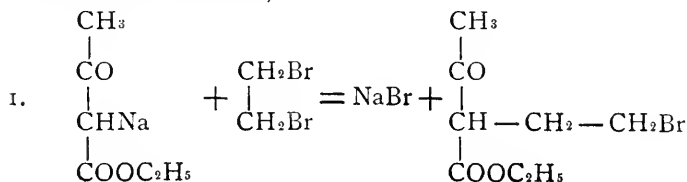
1. Comparing the allyl series with the tetramethylene series, the physical properties of isomeric members of the two series are found to be entirely different.

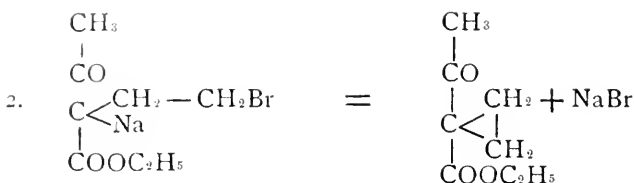
2. The compounds derived from ethyl-acetate and benzoyl-acetate show great stability in the operation of saponification with alkalis, while the isomeric allyl compounds are entirely broken up by similar treatment.

3. Finally, the allyl compounds furnish addition products with bromine, while the tetramethylene compounds produce only substitution products.

Although as yet tetramethylene has not been isolated, nor has an open chain of four carbon atoms been produced from the ring portion of any tetramethylene compound, the author hopes in future to be able to furnish desirable evidence of this character.

Compounds containing closed chains of three carbon atoms were obtained by operating with ethylene bromide upon ethyl aceto- and benzoyl-acetate. Thus in a similar manner to that already described, ethyl aceto-trimethylene-carbonate was produced; the action, as in the case of the analogous tetramethylene compound, taking place in two stages distinguished by successive treatments with sodium, thus:

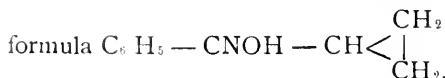




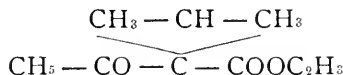
From this compound the acid and a number of salts were prepared. Analogous compounds from ethylene bromide and ethyl benzoyl-acetate were prepared, and in addition benzoyl-trimethylene, $\text{C}_6\text{H}_5 - \text{CO} - \text{CH} < \begin{array}{l} \text{CH}_2 \\ \text{CH}_2 \end{array}$. Acetyl-trimethylene

$\text{CH}_3 - \text{CO} - \text{CH} < \begin{array}{l} \text{CH}_2 \\ \text{CH}_2 \end{array}$ was also prepared, but owing to lack of material was not identified until after the other trimethylene compounds had been described.

The action of hydroxyl-amine upon benzoyl-trimethylene resulted in the formation of benzoyl-trimethylene-oxime, having the following



By treating sodium ethyl acetate with propylene bromide the compound ethyl acetyl-methyl-trimethylene carbonate of the formula



was produced. The formation of this compound shows that the kind of action which results in the formation of trimethylene compounds is of a *general* character, and not limited to one or two initial substances such as ethylene bromide.

The author hopes soon to publish additional papers bearing upon the oxime compounds, the formation of one of which has been mentioned.—(*Berichte der deutschen chemischen Gesellschaft* 16, 208, 1787 and 2136; 17, 1440.)

W. C. D.

On Ferrous Chloride.

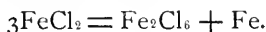
The experiments of Nilson and Pettersson in determining the vapor density of glucinum chloride, an account of which is to be found in the present number of this Journal, have led VICTOR MEYER to repeat the determination of the vapor density of ferrous chloride. Nilson and Pettersson having observed that the vapor of glucinum chloride is capable of corroding glass and porcelain,

Meyer remarks that it has become an important matter to reinvestigate, using platinum vessels only, those metallic chlorides, the determinations of whose vapor densities have been attended with difficulties. A redetermination of the vapor density of ferrous chloride seemed of particular interest, since heretofore it has been an undecided question whether to ascribe to this compound the formula FeCl_2 or Fe_2Cl_3 . For his experiments Meyer used a pure, white specimen of the chloride, a determination of the chlorine in which gave the following figures :

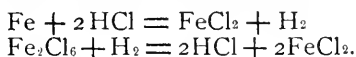
	Found.	Calculated for FeCl_2 .
Cl	55.68	55.90 per cent.

This was further purified by repeated sublimation in a stream of pure and dry hydrochloric acid gas.

It was found furthermore that, if this compound is heated in a difficultly fusible glass tube through which pure nitrogen is passed, most of the compound sublimes unchanged, but that a small quantity of a black residue is left behind, while in the sublimate a minute amount of the green crystals of ferric chloride can be detected. These circumstances were accounted for by assuming that the following reaction takes place :



The correctness of this assumption was supported by the fact that a replacement of the nitrogen atmosphere by one consisting of pure and dry hydrochloric acid gas resulted in effecting the sublimation of the entire quantity of ferrous chloride, leaving no residue and without the appearance of any abnormal body in the sublimate. The action of the hydrochloric acid in preventing the decomposition given above is assumed to be as follows :



In view of the facts just considered, the determination of the vapor density was made in an atmosphere of hydrochloric acid ; the vessel used was the porcelain tube previously recommended by the author.¹ In order to ascertain whether or not the use of the hydrochloric acid atmosphere was justifiable, a test determination of the vapor density of mercuric chloride was made, with a satisfactory result, *i. e.*

	Found.	Calculated for HgCl_2 .
	9.55	9.36

In connection with ferrous chloride it was found that quite a high temperature is necessary for the volatilisation of this substance ; at a red heat it takes place irregularly and very slowly, but at a yellow heat it becomes rapid and the results obtained agree fairly well.

¹ Berichte der deutschen chemischen Gesellschaft 12, 1112.

The densities found are as follows :

I.	II.
6.67	6.38

The calculated values are for FeCl_2 , 4.39 ; for Fe_2Cl_4 , 8.78.

The value found is therefore the mean of the latter figures, and hence for ferrous chloride it seems that—as was proved conclusively by Züblin and Meyer for stannous chloride—this substance at lower temperatures consists of molecules of the formula Fe_2Cl_4 , but that as the temperature rises these break up into molecules represented by the formula FeCl_2 . The temperature reached in the above experiments was not, however, sufficiently high to produce entirely the latter molecular condition.

The author does not yet seem satisfied to leave the subject of the vapor density of ferrous chloride where it now stands, for although sure that when ferrous chloride is volatilised with use of glass and the hydrochloric acid atmosphere the glass is not at all attacked, he is not so confident in regard to the use of porcelain, and therefore expresses himself desirous of having opportunity to make the determination in platinum vessels.—(*Berichte der deutschen chemischen Gesellschaft* 17, 1335.) W. C. D.

The Union of Bodies by Pressure.

Since the last report on this subject¹ W. SPRING has been experimenting with the view of showing that the heat produced by pressure is by no means as great as is generally supposed. In a late article² he states that the only difference between the views of Jannetaz and himself is in the explanation of the cause of combination. Jannetaz claims that the union of bodies by pressure is due to the heat evolved in the very act of compression, whereas he (Spring) claims that the only heat produced is caused by the rubbing of the particles against the walls of the enclosing vessel, and that in the apparatus used in his experiments this friction is reduced to a minimum. He then attempts to prove both theoretically³ and experimentally that his view of the case is the correct one. A temperature of about 1000 degrees, he states, is necessary to fuse bell metal, so that if the shining coating, mentioned by Jannetaz as having been observed on a block of bell metal after compression, was due to the heat evolved by the pressure, the temperature arrived at must have been in the neighborhood of 1000°. Now in all his experiments the limit of contraction was reached before the piston had sunk in the cylinder one millimeter. Taking this as the distance through which the force acts, he shows that an equivalent of heat equal to .0165 calories is produced in effecting a pressure of 7000 atmospheres. This would produce in

¹ This Journal 6, 129.

² *Ibid.* 17, 1215.

³ *Berichte der deutschen chemischen Gesellschaft* 17, 1015.

his cylinder a temperature of only $40^{\circ}.64$, much below the fusing point of any of the substances used. In the calculation maxima are taken, and the above result could never be reached experimentally.

To verify the calculation, phoron, with a fusing point of 28° , was subjected to 7000 atmospheres pressure in a room whose temperature was 19° . Not the slightest indication of fusion was observable. Azoxy-benzene, fusing at 36° , was then tried with a similar result.

Another experiment was then undertaken to show that the friction between the particles of a mixture could not evolve any appreciable amount of heat. Ordinary gunpowder was subjected to 7000 atm. pressure. It formed a compact block, and in no case tried did it explode.

The melting of the bell metal is explained by the fact that Janetaz compressed his filings between two plates, and that no attempt was made to prevent friction between these and the bell metal.

After showing that the union cannot be the result of fusion, Spring undertakes¹ to determine the amounts of the several compounds formed by successive compressions. He took copper, silver and lead, mixed them with sulphur in proportions to form CuS , Cu_2S , Ag_2S and PbS , and subjected the mixtures to pressure. The resulting block was then filed and a portion treated with carbon-bisulphide, and the amount of sulphide formed thus determined. The remaining portion was again subjected to pressure, filed and treated as before. The amounts of the sulphides formed after one, two, four and six compressions were found to be as follows:

	After one compression.	After two.	Four.	Six.
Ag_2S	4.51 per cent.	12.43 per cent.	46.74 per cent.	69.41
PbS	1.32	19.34	28.08	45.54
CuS	8.49	16.95	24.02	34.60
Cu_2S	14.09	28.20	40.08	56.89

The effect of filing was then investigated. A block of the pressed mixture containing 12.43 per cent. of silver sulphide was ground very fine and then examined, when it was found to contain 13.60 per cent.

Other blocks which had been prepared for some time were next examined, to determine the effect of duration of contact. A block composed of silver and sulphur which had been compressed and allowed to stand about a year, was found to contain 41.63 per cent. of sulphide instead of 12.43 per cent. A piece of copper and sulphur after four years contained 20.86 per cent. of cupric sulphide instead of 8.49 per cent.

As a result of the experiments it is shown that while pressure

¹ *Berichte, etc*, **17**, 1218.

exerts a strong influence in the union of bodies, the amount of the compound formed is dependent besides upon the duration of contact of the substances and the intimacy of the mixture, and cannot be accounted for upon the supposition of the evolution of great heat.

It is probable, therefore, that if Jannetaz had worked more carefully to prevent friction in his apparatus, and had subjected his substances to more than one compression, his results would have been more in accord with those of Spring.

W. S. B.

Gallisin, an Unfermentable Substance in Starch-sugar.

C. SCHMITT and A. COBLENZL have made a careful investigation of the unfermentable substances found in commercial starch sugars, and have succeeded in isolating a definite compound to which they give the name gallisin. The method of separation and purification which they made use of is as follows: 5 kilograms of commercial starch sugar were allowed to ferment. At a temperature of 18–20° C. and with a solution containing 20 per cent. the fermentation was complete in 5 to 6 days. It was filtered; the perfectly clear, almost colorless liquid evaporated as far as possible on the water-bath, and the syrup while still warm brought into a good-sized flask. The syrup was then well shaken with a large excess of absolute alcohol, when it became viscous, but did not mix with the alcohol. The latter was poured off, replaced by fresh alcohol and again shaken. When this shaking with alcohol has been repeated several times, the syrup is finally changed to a yellowish-gray mass. This is now brought into a large mortar, and rubbed up under a mixture of alcohol and ether. After some time the whole mass is transformed into a gray powder. It is quickly filtered off with the aid of an aspirator, washed with alcohol and then with ether, and brought under a desiccator with concentrated sulphuric acid. In order to purify the substance it is dissolved in water and treated with bone-black. The solution is then evaporated to a syrup, and this poured into a mixture of equal parts of anhydrous alcohol and ether. In this way the new compound is obtained as a very fine, pure white powder which rapidly settles. It has much the appearance of starch. Under the microscope it is perfectly amorphous. In the air it deliquesces much more rapidly than ignited calcium chloride.

Treated with dilute mineral acids or oxalic acid on the water-bath gallisin is transformed into dextrose. It does not ferment when treated in water solution with fresh yeast. The analyses lead to the formula $C_{12}H_{24}O_{10}$. When treated under pressure with three times its weight of acetic anhydride at 130–140° it dissolves perfectly. From the solution a product was separated which on analysis gave results agreeing with the formula $C_{12}H_{18}O_{10}$.

(C_2H_3O)₆. The substance appears therefore to be hexacetyl-gallisin.

Physiological experiments on lower animals and human beings demonstrated clearly that gallisin has neither directly nor indirectly any injurious effect on the health.—(*Berichte der deutschen chemischen Gesellschaft*, **17**, 1000.)

The Atomic Weight of Glucinum.

A few years ago NILSON and PETTERSON concluded from their experiments on the specific heat of glucinum that the atomic weight of this element is 13.65, and not 9.1 as had generally been assumed. Lothar Meyer attempted to show that their results are capable of a different interpretation, quite in harmony with the atomic weight 9.1. Afterward Nilson replied to Meyer, and, taking into account the specific heats of the oxide and sulphate of glucinum, found confirmation of his view that the atomic weight is 13.65. If this figure is correct, the periodic law receives a serious blow, as with the larger atomic weight, glucinum cannot be fitted into the scheme which is based on the law. Nilson and Petterson have recently determined with great care the specific gravity of glucinum chloride in gas form, and find that it corresponds to the formula $GlCl_2$ in which the atomic weight of the metal is 9.1. They conclude their interesting paper with these words: "In view of these results and the fact that Avogadro's law is without exception in the whole field of chemistry the basis for the conception of the molecule, we must give up the idea formerly held by us that glucinum is a trivalent element, which we were led to by the agreement of the atomic heat ($Gl'''=13.65$) with the law of Dulong, and the numerous analogies between the physical constants (molecular heat and volume) of the compounds of glucinum on the one hand and of the rare metals scandium, erbium, yttrium, &c., on the other. While recognising in this important case the validity of the periodic law, we at the same time call special attention to the peculiar fact that the laws of Dulong and Avogadro lead to exactly opposite conclusions regarding the atomic weight and valence of the element glucinum, a fact which is unparalleled in the field of metallic elements."—(*Berichte der deutschen chemischen Gesellschaft*, **17**, 987.)

Dumas and Würtz.

It is not too late to record the great loss which chemistry has suffered recently in the death of the two leading French chemists, JEAN BAPTISTE ANDRE DUMAS and ADOLF WÜRTZ.

Dumas had reached a good old age, his best work having been done many years ago. His most important investigations were on the *relations of the molecular volumes of aeriform substances*;

and on *types*, in which he showed that the properties of chemical compounds depend not only upon the nature of the elements of which they are composed, but also upon the manner in which these elements are arranged, upon the *type* to which the compound belongs. This investigation on types was very fruitful, and, though Dumas' conception of types was indefinite, and to a considerable extent artificial, our present views regarding the constitution of chemical compounds are based largely upon this conception.

Dumas also did a great deal towards the accurate determination of atomic weights.

Würtz was a much younger man than Dumas, though he was born in 1817. He had long been a leader in the chemical world. Some of his investigations were of fundamental importance, particularly that on the *substituted ammonias*, the preparation of which gave definiteness to the conception of types due to Dumas, and thus led to the idea of valence; and that in the *diatomic alcohols*, in which he discovered glycol, and, comparing this with ordinary alcohol and glycerin, was led to the recognition of the polyatomic radicals, which in turn led to the recognition of the valence of the elements.

Both Würtz and Dumas were voluminous writers. In 1828 Dumas published his "Traité de chimie appliquée aux arts" in eight volumes. Among the many volumes written or edited by Würtz may be mentioned the "Dictionnaire de chimie pure et appliquée," "Theorie atomique," and "Leçons élémentaire de chimie moderne."

A new and valuable feature will be introduced this year in the meetings of the Chemical Section of the American Association for the Advancement of Science. Prof. J. W. Langley, the presiding officer of the section, has selected two topics for discussion, which have been approved by a majority of the members. The topics are:

1. To what extent is the hypothesis of "Valence" or "Atomicity" of value in explaining chemical reactions?
2. What is the best initiatory course of work for students entering upon laboratory practice? What are the best methods of illustrating chemical lectures?

If the meeting is well attended, and the discussions properly introduced, good results will be sure to follow.

AMERICAN CHEMICAL JOURNAL.

Contributions from the Sheffield Laboratory of Yale College.

XX.—ON PALMITIC ACID AND THE PALMITINS.

BY R. H. CHITTENDEN AND HERBERT E. SMITH.

In an attempt to prepare synthetically a palmityl lecithin we have been led, as a preliminary step, to a study of palmitic acid and its glycerin compounds. In the literature of the subject we have found but comparatively few concise statements concerning these bodies, and those frequently contradictory to the results of our experiments, particularly in regard to the synthetical preparation of the three palmitins. Detailed knowledge of these bodies, of the methods to be used in their preparation, and how to accurately determine the content of palmitic acid in these and other compounds containing the palmitic acid radical, was essential to the success of our work. We have, therefore, made a thorough study of these points; and the results, some of which are new and others simply confirmatory of previous discoveries, we present here as an aid to future workers in the same field.

Preparation of Palmitic Acid.

The difficulty of preparing palmitic acid perfectly pure, that is, entirely free from adhering traces of stearic or other acids not differing greatly in solubility, with which the former is so intimately associated in many of both the animal and vegetable fats, has been clearly shown by the laborious work of Heintz.¹ It therefore

¹ Journal für prakt. Chem. 66, 1. Poggendorf's Annalen 92, 429. Watt's Dict. of Chem. 3, 1070.

seemed desirable to use such material as would be most likely to yield the acid at the outset in the purest condition and with the least labor. All of the more common sources of palmitic acid, as palm oil, contain the troublesome olein. The Chinese vegetable tallow from the *Stillingia sebifera*, so thoroughly studied by Maskelyne,¹ while a good source of palmitic acid, likewise contains the objectionable olein. The wax of the *Myrica cerifera* or bayberry tallow, a commercial article easily obtainable, has been shown by Moore² to consist of "about *one-fifth* part of *palmitin*, the remaining *four-fifths* being free palmitic acid with a small quantity of lauric acid, the latter either free or in the state of *laurin*." The latter is present in such small quantity and differs so widely from palmitic acid in solubility, melting point and composition, that it would seem as if no better source of the acid could possibly be obtained. We have, therefore, employed this article in the preparation of the pure acid.

Several pounds of the commercial tallow were saponified with sodium hydroxide, and on cooling the concentrated solution the sodium salts of the two fatty acids floated as a granular mass on the surface of the fluid, separating from the strong lye in the same manner as from a concentrated salt solution. This mass was skimmed off, dissolved in hot water, filtered, and the solution then acidified with dilute sulphuric acid. When cold the palmitic acid, with probably some lauric, was removed as a solid crust. It was then freed from sulphates by thorough washing with hot and cold water, after which it was dissolved in hot 95 per cent. alcohol, filtered while still hot through animal charcoal and then allowed to crystallise by simple cooling. The crystals so obtained were purified by repeated crystallisations from hot alcohol. The comparatively easy solubility of lauric acid in cold alcohol would seem to guarantee its complete separation by one or two crystallisations.

Two distinct preparations of palmitic acid were obtained from the final crystallisation:

A, being the product crystallising from the alcohol by simple cooling.

B, a second crop of crystals obtained by concentrating the filtrate from *A*.

The solubility of palmitic acid in cold alcohol is greater than

¹ Quart. Jour. Chem. Soc. **5**, 1.

² Amer. Jour. Sci. and Arts, 2d Ser., **33**, 313.

would at first appear. Thus we found by experiment that in 100 parts of absolute alcohol (sp. gr. 0.787 at 22° C.) there were dissolved in 24 hours at 19.5° C. 9.209 parts of the acid. When warmed with the absolute alcohol until completely dissolved and then allowed to stand for 24 hours at 19.5° C. there were dissolved (in 100 parts) 9.428 parts of the acid.

Composition of A.

- I. 0.2562 gram gave 0.2877 gram H_2O and 0.7001 gram CO_2 .
 II. 0.2507 gram gave 0.6883 gram CO_2 .
 III. 0.2826 gram gave 0.3228 gram H_2O and 0.7720 gram CO_2 .

Composition of B.

- IV. 0.3388 gram gave 0.3818 gram H_2O and 0.9315 gram CO_2 .
 V. 0.3604 gram gave 0.9872 gram CO_2 .

	A.			B.		Theory.	
	I.	II.	III.	IV.	V.	Palmitic acid.	Lauric acid.
C	74.54	74.88	74.50	75.00	74.71	75.00	72.00
H	12.48		12.69	12.53		12.50	12.00
O	12.98		12.81	12.47		12.50	16.00

It is thus evident that in composition the acid was quite pure. The melting point of the acid, determined in a thin-walled capillary tube, was as follows :

	A.	B.
(a) melted at	61.50° C. and solidified at 59.50° C.	Melted at 61.9° C.
(b) " "	62.05° C.	" 60.05° C.

According to Heintz, pure palmitic acid melts at 62° C. With this acid all of the following experiments were tried.

Quantitative Determination of Palmitic Acid.

Noticeable variations in the methods of determining this acid as given by different authorities would seem to demand some explanation. It is quite evident from our results that while the variations noticed are not great in themselves, on them hinge mainly the accuracy or inaccuracy of the method. We are not concerned here with the separation of palmitic acid from its closely allied neighbor, stearic acid. Fractional precipitation by means of barium and lead salts has always been deemed sufficient to accomplish this, not

only from this one acid, but also from the other fatty acids with which palmitic is frequently associated. Well-defined statements, supported by experimental data, bearing on the precipitation of palmitic acid as a barium or lead salt, we have, however, been unable to find. One would infer from the literature of the subject that such precipitations are complete. It is without doubt true that complete separation of the acid as a barium or lead salt can be effected, but not, we believe, always in a manner suitable for its accurate quantitative determination.

There are apparently in general use two ways of precipitating palmitic acid: 1st, by simply adding a solution of barium chloride, lead acetate or calcium chloride either in water or alcohol to a hot alcoholic solution of the free acid; 2d, by addition of the precipitant to an alcoholic solution of an alkaline salt of the acid. Judging from some descriptions¹ of methods it would appear that this latter point can be most conveniently accomplished by the simple addition of ammonium hydroxide to the boiling alcoholic solution of the free acid until the former is present in slight excess. Addition of the reagent is then followed by precipitation of the acid in combination with the base added. The reasons why precipitations made by either of these methods are liable to give very poor results are to be found in the decomposition of both barium and lead palmitates by water, also by alcohol containing acetic acid, yet washing of the barium palmitate precipitate by water is quite necessary when even a slight excess only of an aqueous solution of barium chloride is added to either an alcoholic or an ammoniacal alcoholic solution. Equally necessary is it to wash the same precipitate with alcohol containing a little acetic acid when previous to precipitation the free fatty acid has been converted into a sodium palmitate by boiling with sodium carbonate, for under such circumstances a trace of sodium carbonate is liable to dissolve in the boiling absolute alcohol used to separate it and thus form barium carbonate. Again, we have found that precipitation of palmitic acid from a hot alcoholic solution by an alcoholic solution of lead acetate, the mixture being allowed to stand in the cold for some time, invariably yields low results, not alone due to the solubility of the lead palmitate in alcohol, but apparently to the decomposing action of the acetic acid liberated by the reaction itself, yet ammonia added even in very small quantity gives a precipitate of lead hydroxide.

¹ Compare Maskelyne. *Jour. Chem. Soc.* 8, 8-9.

All of our determinations of palmitic acid by precipitation with either barium chloride, acetate or lead acetate, followed by ignition and weighing as either barium sulphate or lead oxide, have invariably given us low results, and that in whatever way the precipitation was made. In no case, working with pure palmitic acid, have we succeeded in recovering more than 96 per cent. of the acid.

In Storer's Dictionary of Solubilities only indefinite statements are to be found concerning the palmitates, and we have thus been led to determine the solubility of several of the more insoluble salts of palmitic acid, as well as the action of dilute acetic acid on them. The purity of each salt experimented with was determined by analysis.

Calcium palmitate.

Ca calculated, 7.25 per cent. ; Ca found, 7.14 per cent.

Solubility of the dry salt.—In 100 parts¹ of absolute alcohol (sp. gr. = 0.787 at 22° C.) there was dissolved in 22 hours at 20° C. 0.0103 part of the salt.

Barium palmitate.

Ba calculated, 21.17 per cent. Ba found, 21.19 per cent.

Solubility of the dry salt.—(a) In 100 parts of absolute alcohol there was dissolved in 22 hours at 20° C. 0.0035 part of the salt.

(b) In 100 parts of boiling² absolute alcohol there was dissolved in 6 hours 0.0128 part of the salt.

Solubility of the moist, freshly precipitated salt.—(a) In 100 parts of absolute alcohol there was dissolved in 24 hours at 21° C. 0.0146 part of the salt.

(b) In 100 parts of boiling absolute alcohol there was dissolved in 6 hours 0.0197 part of the salt.

(c) In 100 parts of absolute alcohol, containing 10 drops of acetic acid of sp. gr. 1.051, there was dissolved in 22 hours at 20° C. 0.0334 part of the salt.

(d) In 100 parts of boiling absolute alcohol, containing 10 drops of acetic acid of sp. gr. 1.051, there was dissolved in 6 hours 0.1486 part of the salt.

Magnesium palmitate.

Mg calculated, 4.49 per cent. Mg found, 4.58 per cent.

Solubility of the dry, crystallised salt.—(a) In 100 parts of absolute alcohol there was dissolved in 22 hours at 20° C. 0.0993 part of the salt.

¹ 1 part = 1 gram.

² Evaporation prevented by inverted condenser.

(b) Warmed with absolute alcohol until completely dissolved, and then allowed to stand at 20.5°C . for 24 hours, there was dissolved in 100 parts 0.4869 part of the salt.

Lead palmitate.

Pb calculated, 28.87 per cent. Pb found, 28.45 per cent.

Solubility of the non-crystalline dry salt.—(a) In 100 parts of absolute alcohol there was dissolved in 24 hours at 19°C . 0.0007 part of the salt.

(b) Warmed with absolute alcohol until considerable had dissolved, and then allowed to stand for 24 hours at 19°C ., there was dissolved in 100 parts 0.0027 part of the salt.

Solubility of the freshly precipitated crystalline salt.—(a) In 100 parts of absolute alcohol there was dissolved in 24 hours at 21°C . 0.0033 part of the salt.

(b) Warmed with absolute alcohol, whereby nearly all of the salt was dissolved and then allowed to stand at 21°C . for 24 hours, there was dissolved in 100 parts 0.0157 part of the salt.

(c) In 100 parts of absolute alcohol containing 10 drops of acetic acid, sp. gr. 1.051, there was dissolved in 24 hours at 21°C . 0.0391 part of the salt.

It is hence apparent that in alcohol alone, all of the salts experimented with are somewhat soluble, enough in many cases at least to interfere materially with an accurate determination of the acid. But the greatest source of error is to be found in the solvent action of any free acid present in the mixture. This is plainly shown in the action of acetic acid on both the lead and barium salts. It is, moreover, easily demonstrable that the action of the acid is a decomposing one, breaking up the salt with liberation of the fatty acid. Again, the decomposing action of water is liable to prove an important factor. The action of water on the alkali salts of this acid has long been known,¹ but apparently it has not been, at least generally, considered that the other salts were so affected; thus Maskelyne² directs, in the preparation of the barium salt, that it be washed thoroughly with water. The decomposition, however, takes place very readily, and is easily demonstrated by the fact that the water, either hot or cold, used in washing such a precipitate never ceases to contain either lead or barium, while hot alcohol

¹ Watt's Dictionary of Chemistry 4, 334.

² Journal Chem. Soc. 8, 8-9.

poured over the precipitate so washed, deposits palmitic acid on cooling. The alternate solvent action of the water and alcohol, moreover, continues as long as any of the precipitate remains.

The method which we have finally adopted as the simplest and most accurate for determining palmitic acid, when in combination with glycerin or similar organic bases, is as follows: The first step is naturally a process of saponification. This is accomplished most advantageously by dissolving a weighed portion of the palmityl-containing substance in a small quantity of warm absolute alcohol in a capacious silver crucible, then adding an alcoholic solution of pure potassium hydroxide, and heating the mixture on a water-bath. After boiling gently for a short time the solution is evaporated to dryness. The residue is then dissolved in a little warm water, the solution diluted to 200–250 cc., after which the potassium palmitate is decomposed by the addition of hydrochloric acid. In this manner the acid is precipitated in large white flocks, if the solution was suitably cooled. The mixture is then heated to boiling, the melted acid floating on the surface of the fluid. After standing 24 hours the acid is filtered, washed with water until no further chlorine reaction can be obtained, then dissolved in a little boiling absolute alcohol, and the solution collected in a weighed glass bottle provided with a tightly fitting glass stopper. By evaporation of the alcohol the weight of the acid is easily obtained.

This simple method, which has in it nothing essentially new, has proved by far the most satisfactory of any that we have tried, and certainly there can be no possible fallacy connected with it. Theoretically a small amount of palmitic ether might possibly be formed by evaporation of the alcoholic solution of the acid, but if any is formed it is apparently in too small quantity to materially affect the result. Care, however, must be taken not to dry the palmitic acid residue for too long a time, as oxidation is liable to occur.

Following are some trial experiments with pure palmitic acid:

I. 1.0387 grams yielded after saponification 1.0407 grams acid = 100.19 per cent.

II. 0.4586 gram yielded after saponification 0.4578 gram acid = 99.82 per cent.

III. 0.3218 gram yielded after saponification 0.3234 gram acid = 100.49 per cent.

IV. 0.3807 gram yielded after saponification 0.3812 gram acid = 100.10 per cent.

V. 0.3782 gram yielded after saponification 0.3779 gram acid = 99.92 per cent.

VI. 0.4028 gram yielded after saponification 0.4007 gram acid = 99.47 per cent.

VII. 0.4266 gram yielded after saponification 0.4262 gram acid = 99.90 per cent.

VIII. 0.5518 gram yielded after saponification 0.5505 gram acid = 99.74 per cent.

Synthesis of the Palmitins.

Since Berthelot¹ announced the preparation of the three palmitins by synthesis, and the similarity of the artificially formed tripalmitin with the natural palmitin, but few additional experiments have been recorded confirming his results, or adding new data to those already acquired. By Berthelot's methods, all three of the palmitins can be prepared by simple heating of the free acid, with water-free glycerin for definite periods of time at definite temperatures; the latter, apparently, being more important than either the length of time or the proportion in which the acid and glycerin are mixed, for from Berthelot's description, this alone would appear to govern the production of the desired palmitin. According to the well-known statements² of Berthelot, *monopalmitin* melting at 58° C. and solidifying at 45° C. is formed by heating equal weights of glycerin and palmitic acid for 24 hours at 200° C., *dipalmitin* melting at 59° C. and solidifying at 51° C. by heating equal parts of glycerin and acid at 100° C. for 114 hours. It is likewise formed by heating a mixture of acid and glycerin 7 hours, at 275° C., while *tripalmitin* melting at 60° C. and solidifying at 46° C. is formed by heating monopalmitin for some hours with 10 to 15 times its weight of palmitic acid.

In spite of these definite statements, a large number of experiments lead us to the view that the formation of a *single* palmitin without admixture is rarely accomplished. Much more likely are we to obtain a mixture of all three in variable proportions, separable only by suitable solvents. This Hundeshagen apparently found to be the case in his recent synthetical preparation of the stearins,³ particularly with the mono- and di-stearins. Moreover, the large

¹ Jahresbericht der Chemie 6, 452-453; Journal für prakt. Chemie 58, 412, and 60, 193; Watt's Dict. of Chemistry 4, 335; Chimie Organique 2, 74-77.

² Chimie Organique 2, 75.

³ Journal für prakt. Chemie 28, 224.

excess of glycerin, called for by Berthelot's process, would seem to interfere materially with the object in view, and indeed our own experiments have shown that much better results can be obtained by using the glycerin and palmitic acid in atomic proportions.

In an attempt to prepare monopalmitin by Berthelot's process, 100 grams of palmitic acid, and a like quantity of glycerin (Price's) previously rendered anhydrous by heating at 150° – 180° C. for 4–5 hours, were heated for about 18 hours at 180 – 200° C. in a stoppered retort, the drawn-out end of which dipped under mercury. On being cooled the hardened fat was washed with water to remove adhering glycerin, and then warmed for a short time¹ with a small excess of calcium hydroxide to convert the free palmitic acid into a salt insoluble in ether. The fats freed from lime by washing with water, were dried in the air, and then extracted with warm ether, by the evaporation of which a residue of 51 grams of palmitins was obtained. According to Berthelot, this residue should consist of monopalmitin, since the method of preparation accords very nearly at least with his description. Tested, however, the crude product melted at 61 – 63° C., and began to solidify in fine crystals at 55° C. Analysis, moreover, showed that the dry product contained 91.38 per cent. of palmitic acid, plainly indicating that it was a mixture mainly of di- and tri-palmitin.

An attempt was then made to separate the palmitins by crystallisation from warm alcohol, a method which we have found quite convenient, as the three palmitins differ widely in solubility in this agent. The difference is even greater than we had at first supposed, as the following experiments made later with pure products clearly show.

Solubility of Tripalmitin.

Theoretical amount of palmitic acid in the substance, 95.28 per cent.; found, 95.26 per cent.

(a) In 100 parts of absolute alcohol (sp. gr. 0.787) there was dissolved in 2 hours at 21° C., 0.0053 part of the substance.

(b) Warmed with absolute alcohol until the fat was completely dissolved, then allowed to stand for 2 hours and filtered at 21° C., there was dissolved 0.0043 part of tripalmitin in 100 parts of alcohol.

¹ If heated for longer than 20–30 minutes, there is danger that considerable monopalmitin may be decomposed and the acid saponified.

Solubility of Dipalmitin.

Theoretical amount of palmitic acid in the substance, 90.14 per cent.; found, 90.14 per cent.

(a) In 100 parts of absolute alcohol there was dissolved in 2 hours at 20° C. 0.2097 part of the substance.

Raising the temperature a few degrees increases very greatly the solubility, thus at 27° C. there was dissolved in 2 hours 0.5040 part of dipalmitin in 100 parts of the absolute alcohol.

Solubility of Monopalmitin.

Theoretical amount of palmitic acid, 77.57 per cent.; found, 78.02 per cent.

(a) In 100 parts of absolute alcohol there were dissolved in 2 hours at 21° C. 4.1351 parts of the substance.

(b) Warmed with absolute alcohol until the fat was completely dissolved and then allowed to stand for 2 days at 22.5° C. there were dissolved in 100 parts of alcohol 5.3060 parts of monopalmitin.

Thus while tripalmitin is almost entirely insoluble in cold alcohol, dipalmitin is somewhat soluble and monopalmitin quite easily so. Again tripalmitin dissolves but slowly when warmed with alcohol, except when the latter is in large excess, and hence a mixture of these three bodies may be separated by simple treatment with hot and cold alcohol. Thus from the 51 grams of palmitins obtained by Berthelot's process, as described above, repeated crystallisations and re-crystallisations from alcohol yielded five products.

A, a portion of the fat which crystallised from slightly warm alcohol after the more insoluble tripalmitin had separated and before the more soluble monopalmitin had had a chance to crystallise; obtained constant after five crystallisations, melted at 70.5° C., solid at 66.5° C.

On analysis 1.2009 grams of the substance gave 1.0849 grams palmitic acid = 90.34 per cent. Evidently pure dipalmitin.

B, representing that portion of the palmitins which separated from the warm alcohol before *A*, but after the removal of the greater portion of the tripalmitin. This product made up the greater bulk of the yield, melted at 66.5° C., solid at 64.5° C.

On analysis 0.6286 gram gave 0.5790 gram palmitic acid = 92.10 per cent. This product we shall notice later on.

C, a product more soluble than *B*, obtained from the filtrates during the crystallisations of the latter, melted at 61° C., solid at 57° C.

On analysis (*a*) 0.3714 gram gave 0.3348 gram palmitic acid = 90.14 per cent.

(*b*) 0.4673 gram gave 0.4203 gram acid = 89.94 per cent. Also dipalmitin.

D, the most soluble portion of the palmitins, of which on analysis 0.7499 gram gave 0.6013 gram palmitic acid = 80.18 per cent. It thus approaches within 2.5 per cent. of monopalmitin, enough dipalmitin being mixed with it to raise the percentage.

E, representing the more difficultly soluble residues, melting at 63.5° C. and solidifying at 43° C.

On analysis (*a*) 0.9615 gram gave 0.9158 gram acid = 95.24 per cent.

(*b*) 0.4688 gram gave 0.4467 gram palmitic acid = 95.28 per cent. Hence the product was pure tripalmitin.

A second preparation of palmitins was made with the same amounts of palmitic acid and glycerin as before, but the mixture was heated at 180–200° C. for 45–50 hours. From the evaporation of the ether used in extracting the fats after saponifying with lime, there remained a residue which by treatment with alcohol (hot and cold) was resolved into three portions:

I. Soluble in a moderate bulk of cold alcohol.

II. A product more soluble than I, separating from the united filtrates only after further concentration.

III. An insoluble portion which separated even from a large quantity of alcohol. Little, if any, tripalmitin could be separated.

Products I and II contained respectively 78.70 per cent. and 79.57 per cent. of palmitic acid, thus approaching very nearly to monopalmitin. By recrystallisation of these two products a pure monopalmitin was obtained, melting at 63° C. and solidifying at 62.5° C.

Two analyses were made as follows:

(*a*) 0.8347 gram gave 0.6513 gram palmitic acid = 78.02 per cent.

(*b*) 0.7964 gram gave 0.6246 gram acid = 78.42 per cent.

Product No. III melted at 64.5° C. and solidified at 61° C.

Analysis showed 91.59 and 91.74 per cent. of palmitic acid. This, however, by repeated treatment with alcohol was resolved into two distinct and widely different portions:

A, a heavy crystalline precipitate separating from a large bulk of alcohol, melting at 69° C., solidifying at 62° C.

B, crystallising from the concentrated filtrate from *A*, melted at 49° C., solid at 48° C.

In the filtrate from *B* there were found traces of a body melting at 58° C. and solidifying at 50.5° C.,¹ also a body more insoluble, melting at 61 – 62° C. and solidifying at 53 – 54° C.

Product *B* was again crystallised from hot alcohol. The main bulk of the substance still retained the same melting point of 49° C., solidifying at 48° C. By the crystallisation, however, two small portions of fat were obtained, the more insoluble melting at 64.5° C., solidifying at 62° C., the other melting at 60° C. and solidifying at 52° C.

The body melting at 49° C. gave, on analysis, the following result:

0.4092 gram gave 0.3685 gram palmitic acid = 90.05 per cent.

In composition, then, this body would appear to be pure dipalmitin, although the melting point is much too low for the ordinary form; possibly this compound may represent an isomeric form of the fat.

Product *A* was recrystallised from warm alcohol, the main bulk of the substance retaining the melting point of 68.5 – 69° C., but solidifying at 67.5° C. By this crystallisation a small insoluble residue (oily droplets) was obtained by dissolving in hot alcohol, which melted at 63.5° C. and solidified at 49 – 50° C.; probably mainly tripalmitin. In the filtrate from the main product a small amount of substance melting at 58.5° C. and solidifying at 51.5° C. was obtained; probably dipalmitin.

The main product was now analysed:

0.4742 gram gave 0.4349 gram palmitic acid = 91.71 per cent.

We had here presumably a mixture of one part tripalmitin and three parts dipalmitin, containing theoretically 91.42 per cent. of palmitic acid. We had met with a body of about this composition several times, and it was interesting to ascertain whether the mix-

¹ All of these bodies melting in the neighborhood of 59° C. and solidifying near 51° C. are doubtless slightly impure forms of dipalmitin, although it is quite possible that traces of polyglycerides should be formed by the long heating and the high temperature employed.

ture was a constant and more or less stable one or merely the result of chance. The substance was, therefore, again crystallised from hot alcohol, the middle portion of the yield only being saved. The product still melted at $68-69^{\circ}$ C., and began to solidify in beautiful crystals at 67° , although the crystallisation was not complete until $65-64^{\circ}$ C.

Analysed, the product yielded 91.50 and 91.80 per cent. of palmitic acid.

It is plain, then, that we have to do here with a well-defined mixture of three parts of dipalmitin and one part of tripalmitin, a mixture which would seem to be something more than a mere mechanical union of the two bodies, since repeated crystallisation changes neither the composition nor melting point of the body. In crystallising the substance from hot alcohol, however, it sometimes appeared as if a small portion was broken apart, as it were, the tripalmitin remaining undissolved, while the corresponding amount of dipalmitin was found afterwards in the filtrate.

In solubility this body stands about midway between di- and tripalmitin.

(a) In 100 parts of absolute alcohol there was dissolved in 2 hours at 21.5° C. 0.0860 part of the substance.

(b) Warmed with alcohol until completely dissolved, then allowed to stand for two hours and filtered at 21.5° C., there was dissolved in 100 parts of alcohol 0.1298 part of the substance.

Again, this same body was met with in an attempt to prepare dipalmitin. Here repeated efforts were made, by fractional crystallisation, to separate the two bodies. All five of the fractions, however, melted at about $68.5-70^{\circ}$ C. and solidified at $67-68^{\circ}$ C., while analysis of two of the fractions showed 91.68 per cent. and 91.33 per cent. of palmitic acid respectively, theory requiring 91.42 per cent. In still another case the same body was found with a melting point of 68° C., solidifying at 66° C., and with a content of 91.63 per cent. of palmitic acid.

Again, a large amount of this same mixture was obtained in an attempt to purify a quantity of the palmitins obtained by Berthelot's process, with the same melting point of $69-70^{\circ}$ C., solidifying at 68° C., and with a content of 91.56 per cent. of palmitic acid.

Hundeshagen¹ mentions that in working with the stearins he found it comparatively easy to free distearin from any admixture

¹ Journal für prakt. Chem. 28, 228.

either of stearic acid or of monostearin, but that tristearin could be separated only with extreme difficulty, or not at all. He mentions, moreover, a mixture, which he met with, possessing a melting point of 58° C. and showing on analysis a content of 93.04 per cent. of stearic acid, corresponding to about equal molecules of the two bodies, and that even after repeated crystallisations it showed the same melting point and composition. With the palmitins the only mixture we have met with at all constant is the one already mentioned.

Following Berthelot's plan we attempted the preparation of dipalmitin. Equal weights of water-free glycerin and palmitic acid (30 grams) were heated at a low temperature (about 100° C.) for 114 hours, then treated with lime and extracted with ether. 7 grams of a fat were obtained, melting at $62-63^{\circ}$ C., and solidifying at 55.5° C., with a content of 89.76 per cent. of palmitic acid. The analysis by itself would lead one to suppose that we had here nearly pure dipalmitin, but further investigation showed that such was not the case. By fractional crystallisation from warm alcohol several portions were obtained, one melting at 64° C. and solidifying at 61° C., another melting at $46-50^{\circ}$ C.¹ and solidifying at 45° C. with a content of 91.90 per cent. palmitic acid.

It is thus evident that here as well as in the other cases, in spite of the low temperature employed, all three of the palmitins had been formed, though less tripalmitin than at a higher temperature.

Preparation of the three Palmitins when the Acid and Glycerin are mixed in atomic proportions.

An attempt was now made to see if better results could not be obtained by heating the acid and glycerin in atomic proportions. Three portions of palmitic acid, 30 grams each, were taken, and to each were added the requisite theoretical amounts of pure glycerin for the tri-, di- and mono-palmitin respectively, viz. 3.59 grams, 5.38 grams and 10.77 grams. All three mixtures were heated in small flasks with the tubular end under mercury. They were heated at $180-200^{\circ}$ C. for 4 hours; at the end of which time, or even sooner, there appeared to be no further evidence of chemical action, no more water being evolved. The fats were then heated with lime and extracted with ether.

¹ Appeared to melt at 46° C., but remained so opaque it was hard to determine.

In the case of the tripalmitin a residue of fat was obtained weighing 20 grams, melting at $61-62^{\circ}\text{C}$. and solidifying at $47.5-48^{\circ}\text{C}$. On analysis, 94.14 per cent. of palmitic acid was found. A single extraction with warm alcohol sufficed to remove the admixture of lower palmitins. The tripalmitin so obtained showed on analysis 95.42 per cent. of palmitic acid, theory being 95.28 per cent. This is without doubt the easiest and quickest way of preparing tripalmitin synthetically; the yield large and the product pure.

Evaporation of the ether used in the extraction of the dipalmitin left 13 grams of residue, melting at 62°C . and solidifying at 54°C ., with a content of 92.48 per cent. of palmitic acid. By crystallisation of this product from warm alcohol, and rejecting that which crystallised at first, a pure dipalmitin was obtained, with a content of 90.54 per cent. of palmitic acid. Still the yield was not large.

In the case of the monopalmitin, 10 grams of fat were obtained by evaporation of the ether, melting at $67-68^{\circ}\text{C}$. and solidifying at 59°C . Analysis showed it to contain 91.61 per cent. of palmitic acid, evidently containing a large proportion of di- and tri-palmitin.

It would thus appear from the foregoing a difficult, if not almost impossible, matter to form synthetically either mono- or di-palmitin without a greater or less admixture of tripalmitin, separable, however, by repeated crystallisations. If, however, the palmitic acid and glycerin are heated together at a *low* temperature for a long time, there is without doubt much less tripalmitin formed and apparently less danger of the formation of the three-fourth dipalmitin mixture.

Properties of the pure Palmitins.

Monopalmitin is described by Berthelot as crystallising from ether in needles or microscopic prisms, or in radiating groups with a common centre. Our preparations of monopalmitin showed approximately the same appearance, crystallising from ether in the form of rhombic plates, single and in bunches, sometimes very closely packed; some of the plates with very perfect edges, others serrated. From alcohol (absolute) the palmitin was inclined to separate in small spherules, sometimes aggregated into masses, showing no distinct crystalline form.

The melting point of monopalmitin Berthelot places at 58°C .¹ Observing, however, all of the precautions which he deems so

¹ *Chimie Organique* 2, 75.

necessary to bring the fat into the same molecular state, and which is more essential for the palmitins¹ than the stearins, we have still been unable to obtain a monopalmitin with so low a melting point. All the preparations that we have obtained, with a content of palmitic acid closely accordant with theory, have melted at 63° C., becoming solid at 62.25–62.75° C.

Dipalmitin, Berthelot describes as crystallising in small tables and needles. Our preparations have crystallised from ether in warty masses, in which no distinct crystalline form could be observed. From alcoholic solutions, the fat separated in long curved needles, joined into branching groups with frequently small spherical masses of the fat attached to them.

The dipalmitin of Berthelot melts at 59° C. and solidifies at 51° C. All of our preparations of dipalmitin that possessed the requisite percentage of palmitic acid melted at about 61° C., solidifying at 57° C. Twice, however, we have obtained a palmitin with the theoretical percentage of palmitic acid, but with a constant melting point of 49° C., solidifying in the one instance at about 47° C., the other at 48° C.

Tripalmitin dissolved in hot alcohol, crystallised on cooling from dilute solutions in groups of irregularly shaped crystals. Crystallised from ether, tripalmitin appeared in the shape of irregular, doubly curved bodies, singly and crossed, in groups of two or more; from more dilute solutions frequently appearing in the form of smaller and more closely aggregated bunches.

According to Berthelot, tripalmitin melts at 61° C., and solidifies at 46° C. One sample of tripalmitin that we obtained with a content of 95.14 per cent. of palmitic acid (theory 95.28), had a constant melting point of 62° C., solid at 45.5° C. Several other samples, however, with a percentage amount of palmitic acid closely agreeing with the theoretical, melted a degree or so higher, and solidified two degrees lower; for example, one melting at 63° and solidifying at 45°, still another melting at 64° C., and crystallising at 47° C.

In the case of this tripalmitin we had a very forcible illustration of the phenomena illustrating the isomeric modification of fats so admirably demonstrated by Duffy,² who found a natural tripalmitin in palm oil, with a solidifying point of 45.5° C. and with a melting point of three modifications, viz. 46° C., 61.7° C. and 62.8° C.

¹ *Chimie Organique*, 71, 72.

² *Jour. Chem. Soc.* 5, 197; also *Watt's Dictionary* 2, 879.

In a somewhat similar manner our artificial tripalmitin, melting at 64°C. , on being suddenly plunged into a heated bath, melted then at a temperature much below the original melting point. Thus by *plunging* the fat, which had been previously melted in a capillary tube and then suddenly cooled by exposure to the air, into a bath at different temperatures, it was found that the fat was not melted at 42°C. , nor at 43°C. , but when plunged suddenly into a bath at 45°C. , it quickly became milky, and at 47°C. , quite clear. As the temperature rose it again became solid, and remained so up to 64°C. , when it again melted. On the other hand, when placed in a bath at 43°C. , it did not melt when the temperature was *gradually* raised to 55°C. , though when melted, quickly cooled, and then *plunged* into the same bath at 55°C. it melted at once.

After melting and sudden cooling in a capillary tube as described, the tripalmitin retained this low melting point for some time, even after standing for 24 hours at the ordinary temperature. This apparently constitutes a good illustration of the different physical modifications of the fat, as well as showing another point of similarity between the natural tripalmitin and the artificial body.

Maskelyne¹ likewise had a similar experience. He obtained a natural tripalmitin by the extraction of a vegetable fat with a mixture of alcohol and ether, which after repeated crystallisations showed a solidifying point of 49°C. This preparation he records melted at 50.5°C. , then again became solid, and finally melted and remained so at 66.5°C.

The *three-fourths dipalmitin mixture* when crystallised from an etherial solution, appeared under the microscope in the form of small spherical masses, showing spicules over their surface. Crystallised from alcohol the bunches had the appearance of being composed of needle-shaped crystals, showing, therefore, more of the appearance of dipalmitin than tripalmitin. Hundeshagen² in his mixture of equal parts of di- and tri-stearin, states that the crystalline form of the substance varied from time to time, sometimes having more the appearance of the former, sometimes of the latter.

These many variations in the melting points of the individual fats noticed in our work, while undoubtedly due in part to slight impurities or admixtures, too small for analysis to detect, plainly indicate the existence of various physical modifications.

¹ Jahresbericht der Chemie 8, 520.

² Journal für prakt. Chemie 28, 229.

APPARATUS FOR THE DETERMINATION OF NITROGEN BY THE COPPER OXIDE METHOD, AND COMPARISON OF THIS AND THE RUFFLE METHOD.

BY CHARLES W. DABNEY, JR., AND B. VON HERFF.

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The determination of total nitrogen has become the most important operation which the agricultural chemist has to perform. Such high values are attached to the nitrogenous materials in superphosphates that small variations in the determination of nitrogen will make considerable differences in the valuations. It becomes necessary, thus, for the agricultural analyst to attain the greatest possible accuracy in his rapid routine work. Since the introduction of a great variety of different compounds of nitrogen into fertilizers, this problem has become quite a difficult one, and has caused us to try every new method and every improvement which has been suggested.

The two methods which we shall discuss here have each their merits, and both come reasonably near meeting all these requirements. These are the Ruffle method and the copper oxide, or so-called "absolute," method.

1. *The Ruffle Method.*—We have worked this very nearly as described by its author,¹ using Bohemian glass combustion tubing always, however. We have not tried the method without soda, or without hyposulphite, as has been suggested.

This method has the advantage of being simpler, cheaper and somewhat quicker than the copper oxide method. There are fewer risks to run, fewer combustion tubes break, and for several reasons a much larger per cent. of complete analyses are obtained by it.

The tube we have used was exactly like the ordinary soda-lime combustion tube. Charcoal, free from nitrogen, was obtained, and the mixture with sulphur was weighed out in 2 gram portions. The soda-lime and fused hyposulphite were mixed by eye. In making the combustion a noteworthy precaution is to heat the tube very slowly at first, especially in case of compounds containing high

¹ Journ. Chem. Soc. **39**, 87.

per cents of nitrogen. In some cases the determination may require three hours. If the combustion is too much hastened the results will be too low. Ordinarily we have found that an hour and a half is necessary for making two such determinations together, the weighing and filling the tubes included. Occasionally we have found the final reaction in titrating rather indistinct when this combustion had been made.

2. *The Copper Oxide Method.*—We have followed the method as described by Prof. Johnson¹ in the main. We have not found it necessary to pass oxygen, however, in most cases, and have, therefore, omitted the chlorate of potash from the end of the tube. In mixtures containing a good deal of horn, where resistant cyanogen compounds are formed, this oxygen may be of some aid in completing the combustion.

In analysing compounds rich in nitrogen, and especially those containing much nitrate, the addition of charcoal powder to the substance causes the nitrogen to come off more regularly, and gives generally better results.

For making two analyses together by this method we have found that about two hours are required. This depends, however, chiefly upon how the pump works. In making this estimate of the time required we refer to the pump described below, which never took more than ten minutes to complete the exhaustion.

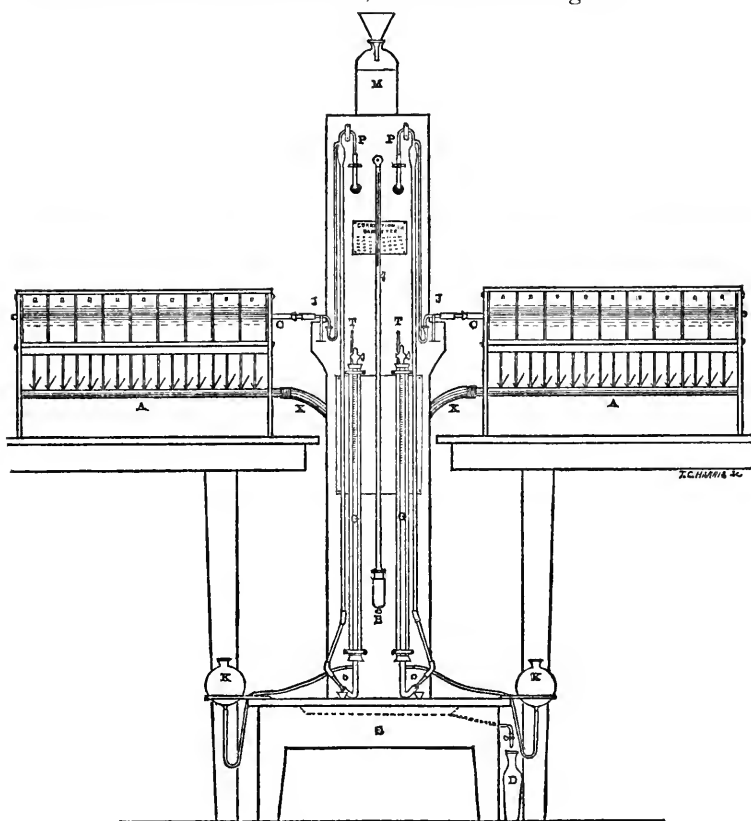
For getting the air, before combustion, and the nitrogen afterwards, out of the tube, we have used carbon dioxide without a pump and have obtained excellent results, though more time is consumed in this way than with a good pump. Magnesite or carbonate of manganese, put in the back end of the tube, are the best sources of carbon dioxide for this purpose. They give off their carbon dioxide slowly and uniformly. Bicarbonate of soda can be used also, though it is liable to give off its gas too suddenly.

In our experience this method of driving the nitrogen out is far preferable to working with a poor, or slow, pump. We recommend it to those who do not want to invest in a Sprengel pump. If you can get a fast-working, tight pump, a combination of both plans of getting the nitrogen out is the best and quickest method.

It was with some difficulty and after numerous trials of pumps of different forms that we got one which met all of the requirements.

¹This Journal 2, 27.

This pump, and the connected apparatus for making two nitrogen determinations at the same time, is shown in the figure.



The only glass part which it is necessary to have made by an expert glass-worker is the piece from P to rubber joint above O and its branch to J, with the ground-glass joint there. The little jet tube in the bulb is wanting in the cut. The length of tube from the bulb to O should be 1.2 m. The length of the branch to J will be regulated to suit the height of your table. The ground joint at J is a great convenience. If a perfect one cannot be obtained, it can be dispensed with and you can get the necessary play in the rubber joint, also indicated at J, which otherwise is omitted. A rubber band over a nail holds the connecting tube firmly into the ground joint.

The speed of the pump will depend much upon the calibre of the jet tube and its relation to that of the fall tube. In our best pump the relation is, internal diameter of the jet tube at smallest place 1.5 mm., internal diameter of fall tube 2.5 mm. The branch tube to J should have an internal diameter of about 2 mm.

The stand to which all of the apparatus is fastened has for its base a shallow box 70 x 70 x 10 cm. on legs, making it 35 cm. high. This is the mercury receiver, and it has an outlet with a pinch-cock at a place convenient for drawing the mercury in the flask D, for returning it to the reservoir M. The front half of the top of this box raises up as a lid. Two holes in the back half of it carry the funnels which catch the mercury. The upright frame is 1.3 m. high above top of base and is well braced behind. It is 25 cm. wide and has two holes at a convenient place for the stout rubber tubes which convey the mercury from the reservoir M to the pumps P P. The flow of mercury is controlled by a pinch-cock just below P. The mercury reservoir, M, is an extra strong 1 gal. aspirator bottle. The tubulature is behind for convenience.

The azotometer with its thermometer T and graduate G, connected with the potash solution reservoir K, which can be raised or lowered as desired, is that of Schiff, figured and described by Prof. Johnson in this Journal.¹ The water connections with the jacket of the azotometer are not figured, because they would complicate the cut, and because it is not necessary to pass water around the nitrogen graduate if one can wait an hour for all the parts to take a uniform temperature before taking the readings.

The barometer is hung conveniently between the pumps. The other details, the connection with the combustion tube C, in the furnace A, and the gas X need no explanation.

The glass parts, described above, were made by our specifications by Mr. Emil Greiner, manufacturer of scientific glass apparatus, 345 E. 18th street, New York city.

A pump of this kind meets all of the requirements of the case. It exhausts the combustion tube rapidly and is easy to manage. It is best to turn on the full head of mercury for the first two minutes and then gradually diminish the pressure by partially cutting off the stream. By evolving some carbon dioxide in the combustion tube after five minutes pumping, the last trace of air can be swept out of the tube in eight to ten minutes. * The follow-

¹ *Loc. cit.*

ing results will illustrate the working of two pumps we have at the N. C. Experiment Station. Two ordinary combustion tubes of equal length were filled as for analysis and connected at ordinary temperature with the pumps, and the amounts of air removed from each in successive minutes were measured under equal temperature and pressure.

Minutes.	Pump No. 1. Cc. of Air Removed.	Pump No. 2. Cc. of Air Removed.
1	65.0	62.0
2	16.0	12.0
3	5.2	3.8
4	0.2	2.9
	<hr/>	
	86.4	
5		1.8
6		1.7
7		0.6
8		0.2
		<hr/>
		85.0

As the careful worker will generally want to make two distinct determinations in each material, this arrangement of two complete and symmetrical sets of apparatus will be found to greatly promote comfort and save time.

Comparative results by the Ruffle and the Copper Oxide Methods.

Using the apparatus and methods described above, we have made a great many comparisons of these two plans of determining nitrogen. The following list of materials is selected to represent a wide range of substances:

1. Paranitrobenzanilid $C_6H_4, NO_2, NH, COC_6H_5 = C_{13}H_{10}N_2O_3$. Well crystallised, pure.

2. Nitrate of potash, KNO_3 , pure, crystallised.

3. Nitrosalicylic acid $C_6H_3, OH, NO_2, COOH = C_7H_5NO_5$. Pure, well crystallised.

4. Dinitrophthalyltoluidid, $C_6H_2, CH_3, (NO_2)_2, N(CO)_2C_6H_4 = C_{15}H_8N_2O_6$.

5. An ammoniated cotton fertilizer, animal ammoniate and a small amount of nitrate of soda.

6. A fertilizer containing tobacco stems and dust (in which we

have found nitrates), fish-scrap, and small amounts of sulphate of ammonia and Peruvian guano.

7. An ammoniated superphosphate, said to contain 1 per cent. of nitrogen from nitrate.

8. A superphosphate ammoniated with animal matter, vegetable matter, and it was said 0.5 per cent. nitrogen from nitrate.

9. Shoemaker's bone meal, from bone extracted with naphtha.

10. Ordinary North Carolina fish-scrap.

11. Cotton-seed meal extracted with naphtha, quite dry and free from oil; from Shoemaker, Philadelphia.

12. Peruvian guano, said to be Chincha Island.

13. Shoemaker's "Ammonite B," mostly extracted muscular tissues of various animals.

14. Dried red blood, from Shoemaker.

Two Ruffle determinations, made at the same time, are given for each substance. The two nitrogen per cents were made by the copper oxide method in duplicate, as described above. All of the determinations in each column were conducted as nearly as possible in the same way. No charcoal was used or oxygen passed in the copper oxide determinations. The results are not all as near together or as near the calculated per cents as they should be, but they serve to show what the methods will do when followed blindly and unvaryingly. When special precautions were used, as the mixture of charcoal directly with nitro compounds, better results were obtained.

In the column of differences between averages of Ruffle results and averages of copper oxide results, Ruffle is + and copper oxide is —. Copper oxide gives results mostly a little higher than Ruffle.

These analyses and many others in our possession show that in fertilizers containing small amounts of nitrogen, the Ruffle method and the copper oxide method give equally good results. By the copper oxide method the errors are apt to be in the direction of too much, by the Ruffle method in the direction of too little.

In substances containing larger amounts of nitrogen the differences are greater. Such substances undoubtedly require special precautions. Highly nitrated compounds should have charcoal or sugar mixed with them, &c.

In general it may be said that the Ruffle method is as well suited

Comparison of Ruffe and Copper Oxide Methods of Determining Nitrogen.—Dabney and von Herff.

Number.	MATERIAL.	RUFFLE METHOD.			COPPER OXIDE METHOD.			Difference between Ruffe and Copper Oxide.	Nitrogen Calculated.	Error by Ruffe Method.	Error by Copper Oxide Method.
		Nitrogen per cent.	Difference.	Average.	Nitrogen per cent.	Difference.	Average.				
1	Paranitrobenzanilid.....	11.45 } 11.54 }	0.09	11.495	11.70 } 11.64 }	0.06	11.670	— 0.175	11.570	— 0.075	+ 0.100
2	Nitrate of potash	13.75 } 13.72 }	0.03	13.735	13.65 } 13.75 }	0.10	13.70	+ 0.035	13.861	— 0.126	— 0.161
3	Nitrosalicylic acid.....	7.50 } 7.40 }	0.10	7.450	7.69 } 7.62 }	0.07	7.655	— 0.205	7.690	— 0.24	— 0.04
4	Dinitrophenyltoluidid.....	12.59 } 12.65 }	0.06	12.620	12.85 } 12.97 }	0.12	12.910	— 0.29	12.844	— 0.224	+ 0.066
5	Ammoniated cotton fertilizer.....	2.10 } 2.07 }	0.03	2.085	2.06 } 2.07 }	0.01	2.065	+ 0.020			
6	Fertilizer, with tobacco refuse.....	2.10 } 2.15 }	0.05	2.125	2.21 } 2.18 }	0.03	2.195	— 0.07			
7	Ammoniated superphosphate with 1 p. c. N from nitrate.....	2.10 } 2.12 }	0.02	2.110	2.11 } 2.04 }	0.07	2.075	+ 0.035			
8	Ammoniated superphosphate with animal and vegetable matter and nitrate ..	2.10 } 2.06 }	0.04	2.080	2.08 } 2.11 }	0.03	2.095	— 0.015			
9	Shoemaker's bone meal	6.74 } 6.69 }	0.05	6.715	6.73 } 6.82 }	0.09	6.775	— 0.060			
10	N. C. fish-scrap	7.52 } 7.49 }	0.03	7.515	7.64 } 7.71 }	0.06	7.675	— 0.160			
11	Cotton-seed meal, extracted.....	7.79 } 7.94 }	0.15	7.865	8.06 } 8.09 }	0.03	8.075	— 0.210			
12	Chincha Island Peruvian	7.21 } 7.30 }	0.09	7.255	7.27 } 7.27 }	0.00	7.270	— 0.015			
13	Shoemaker's "Ammonite B"	12.65 } 12.72 }	0.07	12.685	12.73 } 12.71 }	0.02	12.725	— 0.035			
14	Dried blood.....	14.60 } 14.57 }	0.03	14.585	14.85 } 14.69 }	0.16	14.770	— 0.185			

to the general uses of the chemical laboratory as the copper oxide, or so-called "absolute" method. The latter method, with the aid of the apparatus described above, leaves, however, little to be desired, so that it may be said now that we have two almost equally available and convenient "absolute" methods which can be used to check each other.

CONTINUOUS ETHERIFICATION.

BY L. M. NORTON AND C. O. PRESCOTT.

Since the examination of the process of continuous etherification by Williamson,¹ and the explanation of it in his classical research, our knowledge of its possible applications has made no material progress. The formation of ethers by the action of sulphuric acid upon alcohols has found practical application only in the manufacture of ethyl ether in the manner proposed by Boullay² before the course of the reaction was understood, and in the manufacture of methyl ether,³ which is now used extensively for cooling purposes. We have re-examined the formation of ethyl ether by this process in order to fix more carefully the limits of temperature within which the reaction can be effected, and also the temperature at which etherification is most complete, and we have also investigated the behavior of propyl, isobutyl and isoamyl alcohols when subjected to the process of etherification. We have examined also the formation of mixed ethers by this process.

Ethyl Alcohol.

The apparatus used in all the experiments described below was essentially that originated by Boullay, and afterward used by Williamson. It consists of a two-litre flask, with a wide mouth closed by a cork through which passes a thermometer, a drop-

¹ Ann. d. Chem. **77**, 37, and **81**, 73. ² Jour. Phar. **1**, 96. ³ Tellier, Arch. Phar. **16**, 57.

funnel, and a delivery tube leading to a condenser cooled continually with ice water.

In the first series of experiments 200 grams of commercial 90 per cent. alcohol were subjected to etherification in each experiment. Twenty grams of alcohol were mixed with 36 grams of ordinary strong sulphuric acid, placed in the flask, which was then heated to the desired temperature in an oil-bath, and the mixture was maintained at the desired temperature while the remaining alcohol was slowly added through the drop-funnel. It is evident that if the distillate was subjected to fractional condensation and the undecomposed alcohol returned to the generating flask and only the ether collected, in sufficient time the alcohol would be changed to ether, even at a temperature far too low for advantageous etherification. As we desired to examine the amount of alcohol changed to ether at different temperatures we allowed the ether and undecomposed alcohol to distill together from the generating flask, and subsequently subjected the distillate to fractionation. The distillates from temperatures below 160° were free from sulphurous anhydride. They were treated with solid caustic potash to remove any traces of sulphuric acid and then distilled from quick-lime. After three fractionations, the portions boiling between 35° and 45° were weighed. In these experiments 163 grams of pure ethyl alcohol were available for etherification.

Temperature of formation.	Weight of ether obtained.	Per cent. of theoretical yield of ether.
120° – 125°	12 grams.	7.35 per cent.
125° – 130°	27 “	16.55 “
130° – 135°	45 “	27.58 “
135° – 140°	45 “	27.58 “
140° – 145°	47 “	28.81 “
145° – 150°	47 “	28.81 “

A second series of experiments was now made, and the distillates were fractionated with the utmost care. In these experiments 150 grams of 90 per cent. alcohol were used, and 118 grams of ethyl alcohol were available for etherification. The specific gravity of the ether obtained was 0.744 at 0° compared with water at the same temperature. This specific gravity would indicate the presence of a minute quantity of alcohol in the ether.

Temperature of formation.	Weight of ether obtained.	Per cent. of theoretical yield of ether.
115°-120°	5 grams.	4.2 per cent.
120°-125°	10 "	8.4 "
125°-130°	20 "	16.8 "
130°-135°	33 "	27.7 "
135°-140°	43 "	36.1 "
140°-145°	52 "	43.6 "
145°-150°	47 "	39.5 "
150°-155°	49 "	41.0 "
155°-160°	48 "	40.3 "
160°-165°	? "	

These results would indicate that the action of alcohol upon ethylsulphuric acid begins at a temperature much lower than has been supposed, rises in rapidity and completeness until the temperature of 145° is reached, where the maximum yield of ether is obtained. Above 150° the yield begins to lessen, and doubtless the formation of ethylene begins, but the yield does not diminish greatly until 160° is reached. At 160° the formation of sulphurous anhydride begins and numerous gaseous products are evolved, and the sulphuric acid is soon destroyed, as has been observed by others.¹ Ether continues to be formed above 160° in small quantities, and, according to Mitscherlich,² is even found among products formed at 200° and above that temperature.

Propyl Alcohol.

We were unable to find any evidence that this alcohol was ever subjected to the process of continuous etherification. We took 50 grams of propyl alcohol for our experiment. Fifteen grams were mixed with 20 grams of sulphuric acid, the mixture heated at 135°, and the remaining alcohol added in the usual way. A colorless distillate was obtained, at the same time there was a slight evolution of sulphurous anhydride and a slight deposition of tar in the generating flask. The distillate was treated with solid caustic potash, then distilled from lime, and was found to boil between 80° and 90°. It was next washed with water, distilled again from lime, and then allowed to stand with sodium until all action ceased. Its boiling point was then between 82° and 84°; it possessed a strong

¹ Gmelin, Handbuch 4, 552.

² Ann. Ch. Phys. 3, 7, 12.

etherial odor, and agreed in all respects with the propyl ether described by Chancel¹ and Linneman.² The yield is very good, and this method will prove the most convenient for the preparation of propyl ether.

Isobutyl Alcohol.

It is well known³ that at a high temperature sulphuric acid withdraws water from isobutyl alcohol and produces isobutylene. We have subjected isobutyl alcohol to the ordinary process of continuous etherification at 120° and also at 135°. In both cases sulphurous anhydride was freely evolved, and tar remained in the generator.

A yellowish distillate was obtained, which upon purification and fractionation proved to consist of undecomposed isobutyl alcohol. We were unable to obtain any appreciable quantity of isobutyl ether.

Isoamyl Alcohol.

We next investigated the behavior of isoamyl alcohol under the ordinary conditions of continuous etherification. At temperatures very little above 100° a violent action begins, and sulphurous anhydride is freely evolved. Before the temperature of 140° can be reached the sulphuric acid is destroyed, and only tar remains in the generator. As isoamyl ether boils at 176° it is evident that it cannot be produced by this method. Below 140° a distillate was obtained, which proved to contain undecomposed isoamyl alcohol and hydrocarbons of the C_nH_{2n} series. We were unable to confirm the statement of Balard⁴ that small quantities of isoamyl ether are formed by the action of sulphuric acid upon isoamyl alcohol.

Methyl and Ethyl Alcohols.

The authority for the statement that mixed ethers can be obtained by the process of continuous etherification rests upon two experiments of Williamson.⁵ It seemed desirable to test the applicability of this process to the formation of mixed ethers anew, especially as Gutlrie⁶ was unable to repeat one of Williamson's experiments. We chose for an experiment a mixture of methyl and ethyl

¹ Ann. d. Chem. **151**, 304.

³ Lermontoff, Ann. d. Chem. **196**, 117, *et al.*

⁵ Ann. d. Chem. **81**, 77.

² Linneman, Ann. d. Chem. **161**, 37.

⁴ Ann. d. Chem. et Phys. **3**, 12, 294.

⁶ Ann. d. Chem. **105**, 57.

alcohols, containing 1 mol. of CH_3OH to 1 mol. of $\text{C}_2\text{H}_5\text{OH}$. This mixture was treated in the usual manner at 140° , and the utmost care observed in condensing the products. A colorless distillate, free from sulphurous anhydride, was obtained, and at the same time a gas, which we were unable to condense, escaped from the apparatus. This gas possessed a strong ethereal odor, and was doubtless methyl ether, which boils at -23° . The distillate resolved itself upon fractionation into three portions, one boiling from 10° – 15° , the second from 30° – 40° , and a third portion consisting of undecomposed alcohols. We obtained from the portion boiling lowest a considerable quantity of a liquid boiling between 10° and 13° , possessing a strong ethereal odor, and corresponding in every respect with the methyl-ethyl ether prepared by Williamson¹ from sodium alcoholate and methyl iodide, and also by Würtz,² by the action of a mixture of methyl iodide and ethyl iodide upon silver oxide. The portion of the distillate boiling between 30° and 40° consisted mainly of ethyl ether. The yield of the mixed ether was very good. The three possible ethers appear to be formed simultaneously, but the mixed ether is formed in much the largest proportion.

Ethyl and Propyl Alcohols.

A mixture of equivalent parts of these alcohols was next treated in the usual manner. A colorless liquid was obtained, which resolved itself upon fractionation into ethyl ether, a mixture of ethyl and propyl alcohols, and a portion boiling between 60° – 80° . The portion boiling between 60° and 80° was washed with water, distilled from quick-lime, and finally treated with an excess of sodium to remove any alcohols present, and rectified. The liquid then boiled between 66° and 68° , and possessed an ethereal odor, and gave the following results upon analysis: 0.2286 gram of substance furnished 0.5620 gram of CO_2 and 0.2827 gram of H_2O .

	Theory for $\text{C}_3\text{H}_7\text{OC}_2\text{H}_5$.	Found.
C	68.17	67.04
H	13.64	13.74

The analysis leaves no doubt that the substance is the ethyl-propyl ether which was first prepared by Chancel³ by the action of ethyl iodide upon propyl alcohol and caustic potash.

¹ Ann. d. Chem., **81**, 77.

² Ann. Ch. Phys. **3**, 46, 222.

³ Zeit. f. Chem., 1869, 367.

Ethyl and Isobutyl Alcohols.

Equivalent parts of these alcohols were subjected to the usual treatment. Sulphurous anhydride was freely evolved, and a yellow distillate with a very disagreeable odor obtained. The distillate consisted almost entirely of undecomposed alcohols and no ether could be obtained from it. The mixture behaved exactly as did the isobutyl alcohol alone.

Methyl and Isoamyl Alcohols.

Methylisoamyl ether was prepared by Williamson¹ by the continuous etherification of a mixture of these alcohols. We repeated his experiments, following his directions with the utmost exactness. Sulphurous anhydride was evolved in large quantities. In the distillate obtained we found undecomposed alcohols and products similar to those obtained from isoamyl alcohol alone under like conditions, but were unable to detect the presence of methylisoamyl ether. We made repeated attempts at 135° and 140°, but the distillate in every case consisted almost entirely of the alcohols which had distilled undecomposed as soon as the sulphuric acid had been all reduced. An attempt by Guthrie² to obtain ethylisoamyl ether by continuous etherification, in the manner described by Williamson, gave similar results, and Guthrie was unable to obtain the ether by this method. As our experiments show that etherification does not take place to any extent, certainly in the case of ethyl alcohol, below 105°, and as isoamyl alcohol decomposed sulphuric acid with the evolution of sulphurous anhydride at that temperature, it is evident that the ordinary process of continuous etherification can only be applied to the formation of the simple and mixed ethers from the simplest alcohols, and it is not probable that it can be used satisfactorily for the etherification of alcohols containing more than three atoms of carbon.

MASS. INSTITUTE OF TECHNOLOGY, BOSTON.

¹ Ann. d. Chem. 81, 77.

² Ann. d. Chem. 105, 37.

Communications from the Chemical Laboratory of Rutgers College.

XIII.—NOTE ON OZOCERITE.

BY FRANKLIN S. SMITH.

In the clay fields of Mr. Otto Ernst, of South Amboy, N. J., specimens of Ozocerite have recently been found. In a letter, Mr. Ernst writes: "I do not think it likely that I shall find any paying quantities of it, though I recollect finding a lump ten times as large some years ago. Its low specific gravity probably carried it here by waters from the petroleum fields."

The specimen was in the form of an irregular lump, about three-quarters of an inch in its longest diameter. The color was nearly pure.

A combustion gave:

		Calc. for C_5H_{10} .
Carbon	86.46	85.71
Hydrogen	12.83	14.29
	<hr/>	
	99.29	

The substance was not purified, so that the above results are, of course, only approximate. There is little doubt, however, that the hydrocarbons belongs to the series C_nH_{2n} as stated by Grabowski.

XIV.—NOTE ON SILICIOUS EARTH.

BY J. W. MCKELVEY.

In a small basin on the farm of Mr. D. Judson Cook, which is located near Drakesville, Morris County, New Jersey, there is a deposit of infusorial earth which covers about three acres. The first stratum, which begins at the surface, is peaty to a depth of about one foot. The next is infusorial earth to a depth of three feet, and then come seven feet of a white, sandy clay. At the bottom of this there is a deposit of gravel and cobble-stone drift. The white clay seems to be a mixture of clay and infusorial earth. Near the edge of the bed it grows thin, and the upper fifteen inches of the three feet layer are more porous than the rest.

This infusorial earth is of a grayish-white color, and on igniting becomes perfectly white. It contains small fragments of leaves and twigs.

The specific gravity of the sample was 1.11. On analysis it gave:

Silica	80.66 per cent.
Alumina	3.84
Lime	.58
Loss on ignition	14.01
	<hr/>
	99.09

NEW BRUNSWICK, N. J.

ANTHRACENE FROM WATER-GAS TAR.

BY ARTHUR H. ELLIOTT.

The presence of aromatic hydrocarbons in the products resulting from the destructive distillation of petroleum and its allies has been proved by quite a number of experimenters. L. Prunier¹ treated the products of the distillation of petroleum with bromine, and found that those coming off at low temperatures did not absorb this element, while the products coming off at higher temperatures readily absorbed it, and contained the aromatic hydrocarbons, anthracene, pyrene, chrysene, fluoranthrene, acenaphthene, petrocene and carbpetrocene, together with ethylenes and acetylenes.

Liebermann and Burg² found that by passing the heavy oils resulting from petroleum and paraffine refining through red-hot tubes they obtained a mixture of hydrocarbons similar to ordinary coal tar, and containing four per cent. of benzol and toluol with nine-tenths of one per cent. of crude anthracene. Petroleum yielded benzol but no anthracene. Salzmann and Wichelhaus³ obtained similar results.

All these experimenters worked upon the products of destructive distillation carried on in small apparatus in the laboratory. But the

¹ Ann. Chim. Phys. (5), **17**, 5. Jour. Chem. Soc. **36**, 1025.

² Berichte deutsch. chem. Ges. 1878, 723.

³ Berichte deutsch. chem. Ges. 1878, 802 and 1431.

tar produced by passing heavy petroleum over wood heated to redness on a large scale, was examined by Letny.¹ After several passages through the red-hot tubes it was found that the tar contained benzol, toluol, xyol, naphthalene, anthracene, phenanthrene, and unchanged petroleum. By passing heavy petroleum through a small tube heated to redness and filled with charcoal Letny obtained amylene, benzol, toluol, xylol, and oils boiling at higher temperatures, but no solid hydrocarbons.

Rudnew² says, that at the Kasan Gas Works the tar resulting from the manufacture of petroleum gas is distilled in the ordinary way. It yields ten to twenty per cent. of benzol, and five per cent. of naphthalene, together with anthracene; but he does not give the percentage of the latter.

A little more than a year ago I obtained some of the tar formed during the manufacture of so-called water-gas. It was already known to me that this tar contained naphthalene in very large quantities, and it appeared most probable that other hydrocarbons of the aromatic series were also present, more especially anthracene. Since anthracene is the most valuable of the higher members of the aromatic hydrocarbons, from its use in the production of alizarine—and the day is not far distant when water-gas will be used more extensively, at least in the United States—the value of water-gas tar for the manufacture of anthracene appeared to me of considerable importance. My first efforts were confined to the distillation of the tar, and an examination of that part of the distillate that comes over at 210° to 350° Celsius. This distillate was dissolved in glacial acetic acid, and gave a clear solution; which was treated with a mixture of chromic acid dissolved in a mixture of acetic acid and water, according to the well-known method of Lück. After digesting some hours, the mixture was poured into water and a flocculent precipitate separated. This precipitate having all the appearance of anthraquinone, was thoroughly washed with water, then with dilute solution of sodic hydrate, and finally with water again. The result of this experiment was that that part of the tar distillate coming over between 210°–350° contained 5.8 per cent. of anthracene.

The distillation which gave the above results was continued still further until the contents of the retort became coked. The distillate thus obtained was treated with glacial acetic acid the same as

¹ Ding. Jour. **229**, 353.

² *Ibid.* **239**, 72.

the above ; but only 32.7 per cent. of it was dissolved. The resulting solution was treated with chromic acid dissolved in acetic acid as described before, and the anthraquinone obtained was equal to 2.08 per cent of anthracene in the distillate obtained from 350° Celsius to coking.

In the next experiment I took a measured quantity of tar, 340 cubic centimetres, and obtained a small quantity of oil distilling over below 200° Celsius. The distillation was continued until the contents of the retort were thick pitch. This gave a distillate which was a mixture of oil and solid crystalline matter, amounting to 52.9 per cent. of the original tar. The oil was carefully poured off from the solid part of the distillate, and the latter was treated with petroleum spirit (boiling point 65°–105° C.). The solids thus washed were of a pale yellow color and equal to 3.97 per cent. of the original tar. These solids were dissolved in glacial acetic acid, and treated with chromic acid in the manner before stated. The resulting anthraquinone was equal to 2.90 per cent. of anthracene in the original tar.

From these experiments it became evident that this tar was particularly rich in anthracene, and I determined to pursue the experiments still further, but time did not permit until this summer, when I have again made an examination of quite a number of tars from the manufacture of water-gas.

These tars have a specific gravity ranging from 1.080 to 1.100, are liquid at summer temperatures, and more or less solid during the winter.

Taking one of the dense tars the following results were obtained : The specific gravity was 1.100. For distillation 400 cubic centimetres were taken, and gave the following fractions and weights per hundred volumes of tar distilled :

Temperature, Degrees Celsius.			Weight of Distillate from 100 volumes.	
80 to 200	9.2	{ $\frac{1}{3}$ Oil. $\frac{2}{3}$ Water.
200 " 270	{ 11.2 Solid. 17.7 Oil.	
270 " Pitch	{ 6.0 Solid. 26.5 Oil.	
Last fraction	{ 1.7 Semi-solid. 6.0 Oil.	
Total			78.3	

The fraction coming over between 80 and 200 degrees consisted of a mixture of oil and water, and was reserved for future examination. The second fraction between 200 and 270 degrees Celsius was filtered and the oil pressed from the solid part between sheets of filter paper. The pressed solids were crystalline, and were dissolved in glacial acetic acid and treated with chromic acid according to the method of Lück. This gave only .82 per cent. of anthracene, which is equivalent to .09 per cent. on the original tar. The oil from these pressed solids had a specific gravity of 1.030; it was not examined for anthracene because the pressed solids had given so little of this hydrocarbon. The pressed solids are practically all naphthalene, and the oil yields no phenol when treated with alkalies.

The third fraction coming over at 270 degrees to near the end of the distillation was filtered and the oil pressed out with filter paper as in the case of the second fraction. The pressed solids were of a greenish-yellow color and of low melting point. They were treated with about four times their weight of petroleum naphtha (boiling point between 65 and 105 degrees Celsius) to obtain crude anthracene. This crude anthracene had a melting point of 155° Celsius, and was equal to 18.6 per cent. of the pressed solids. By treatment with chromic and acetic acids it was found to contain 85.1 per cent. of its weight of pure anthracene, which is equal to 15.83 per cent. on the pressed solids. But an examination of the wash petroleum naphtha showed that much anthracene had gone into solution, therefore a direct determination of anthracene in the pressed solids was made, without previous treatment with petroleum naphtha. It was now found that the pressed solids really contained 25.6 per cent. of pure anthracene, which is equivalent to 1.54 per cent. on the original tar.

The oil from the pressed solids of the distillate coming over above 270° had a specific gravity of 1.080, and by treatment with acetic and chromic acids gave 3.0 per cent. of pure anthracene, which is equivalent to 0.79 per cent. on the original tar.

The last fraction was obtained only a few minutes before stopping the distillation and when the contents of the retort were in a viscous condition. This fraction was filtered, and the crystalline mass of oil and solids left on the filter was treated with petroleum naphtha; the amount being too small to submit it to pressure with filter paper. By this treatment the semi-solids

gave 2.0 per cent. of their weight of crude anthracene, which is equivalent to 0.15 per cent. on the original tar. This crude anthracene had a bright orange color, but was too small to submit to the chromic acid treatment. The oil from the last fraction was treated with chromic and acetic acids, and gave 1.81 per cent. of its weight of pure anthracene, which is equivalent to .11 per cent. on the original tar.

The anthraquinone resulting from the treatment with chromic acid had all the properties necessary to its identification. It was of a pure white color, melted at 272° Celsius, and gave beautifully fine crystalline needles by sublimation, and also by solution in benzol. Analysis gave 80.08 per cent. of carbon and 5.14 per cent. of hydrogen; theory requiring 80.77 per cent. of carbon and 4.76 per cent. of hydrogen. This analysis is not as good as it should be, and the small quantity of material at my disposal is the only reason for presenting it. Nevertheless it is sufficiently close to help to identify the anthraquinone in connection with the other properties mentioned and the circumstances of formation.

The total anthracene obtained was equal to 2.63 per cent. on the original tar.

Former experimenters on this class of tars have been satisfied to simply detect the presence of anthracene, or, as in the case of Liebermann and Burg, to record the crude anthracene found. These last gentlemen found 0.9 per cent. in tar obtained from heavy oils from petroleum refining, and assuming that this crude anthracene contained 50 per cent. of pure hydrocarbon, the result is only 0.45 per cent. on the tar they used. Ordinary coal tar obtained in the destructive distillation of bituminous coal for gas contains only 0.3 to 0.4 per cent. of anthracene, while the tar I have described contains four or five times that amount.

Perhaps the most interesting fact in connection with this water-gas tar is that it is the result of the destructive distillation of light petroleum naphtha. This naphtha consists of those members of the marsh-gas series of hydrocarbons boiling below 150° , and consequently entirely free from the more or less solid paraffines found in the heavy oils used by other experimenters.

As time permits I hope to examine these tars still further, and at some future date will give an account of other constituents.

ON THE ACTION OF SODIUM PHENYLSULPHINATE ON METHYLENE IODIDE.

BY ARTHUR MICHAEL AND GEORGE M. PALMER.

In the continuation of a research¹ on the influence of acid radicals containing sulphur on the hydrogen of the adjacent methylene, we endeavored to prepare methylenephénylsulphone by the action of sodium phenylsulphinate on methylene iodide. These experiments led to very unexpected results, which we deem of sufficient interest to describe in a separate note.

To an alcoholic solution of 8 grams (2 mols.) of phenylsulphinic acid, 1.4 grams (1 mol.) of sodium dissolved in absolute alcohol was added, and 7.4 grams (1 mol.) of methylene iodide. The mixture was heated in a flask, connected with a reversed cooler, for four hours on a water-bath. An examination of the contents of the flask showed that no reaction took place under the above-described conditions.

We then made a number of experiments on heating the same mixture in sealed tubes at a higher temperature, and found that a reaction ensued, and was completed by heating four or five hours at 120°. The contents of the tubes were brought in an evaporating dish, the alcohol driven off, and water added to the residue. The oil which separated on addition of water soon solidified, and the substance, after being pressed between bibulous paper, crystallised from alcohol. The substance contained iodine and sulphur. The analyses gave the following results:

I. 0.5070 gram of substance gave 0.1152 gram of H₂O, and 0.5587 of CO₂.

II. 0.3120 gram of substance gave 0.2715 gram of BaSO₄ (Russel's method).

III. 0.2584 gram of substance gave 0.2260 gram of BaSO₄ (Russel's method).

IV. 0.5147 gram of substance gave 0.5083 gram of BaSO₄.

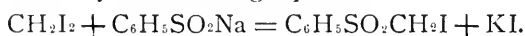
V. 0.2105 gram of substance gave 0.1740 gram of AgI. (After Carius.)

VI. 0.3375 gram of substance gave 0.2815 gram of AgI. (After Carius.)

¹This Journal 5, 116.

	Theory for $C_6H_5SO_2CH_2I$.	I.	II.	Found, III.	IV.	V.	VI.
C	29.8	30.0					
H	2.4	2.5					
S	11.3		11.9	11.7	11.7		
I	45.0					44.7	45.

These results prove that the compound obtained by heating sodium phenylsulphinate with methylene iodide under the above-mentioned conditions, is formed by the replacement of one of the iodine atoms of the latter compound by phenylsulphone, a reaction represented by the following equation:



Methylene-iodophenylsulphone crystallises from alcohol as rhombic prisms with truncated end faces, melting at 64.5° . It is insoluble in boiling water, somewhat soluble in cold alcohol, readily in hot ether, and benzene dissolves it readily in the cold. It is evident that but one-half of the sodium phenylsulphinate employed in the above experiments entered into the reaction, and the following experiment shows that the iodo-sulphone is also formed when the sodium salt and methylene iodide are used in the proportion of their molecular weights.

Four grams (1 mol.) of $C_6H_5SO_2H$, 0.7 gram of sodium dissolved in alcohol and 7.4 grams (1 mol.) of methylene iodide were heated in a sealed tube at 120° and the contents of the tube treated in the above-described manner. We obtained a very good yield of methylene-iodosulphone, melting at 64.5° .

We next endeavored to effect the complete replacement of the iodine of methylene-iodide by phenylsulphone by heating an alcoholic solution of sodiumsulphinate and iodide, in the proportion of two equivalents of the first to one of the latter, at higher temperatures, and here too we met with very unexpected results.

This solution was heated in a sealed tube to 140° without any reaction taking place. Heated to 180° for several hours, the contents of the tube were brought into an evaporating dish and heated until the alcohol was driven off. The residue was extracted with water, and the insoluble portion crystallised several times from alcohol. The substance does not contain iodine.

The analyses gave the following results:

0.2559 gram of substance gave 0.4979 gram of CO_2 and 0.1370 gram of H_2O .

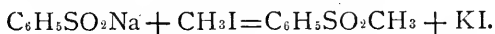
0.2355 gram of substance gave 0.4590 gram of CO_2 and .1109 gram of H_2O .

	Theory for $\text{C}_6\text{H}_5\text{SO}_2\text{CH}_3$.	I.	Found. II.
C	53.8	53.5	53.3
H	5.1	5.9	5.2

The substance crystallises from hot water as large tabular plates, melting at 88° . It is very soluble in cold benzene, alcohol and acetic ether, insoluble in cold water and alkalis. This substance is formed from methylene-iodophenylsulphone by the replacement of iodine by hydrogen, and, as we have shown further on by its synthesis, is methylphenylsulphone. The same compound is obtained in the action of sodium phenylsulphinate on methylene-iodophenylsulphone. An alcoholic solution of these substances, in equivalent proportions, gave a good yield of methylphenylsulphone when heated in a sealed tube at 180° .

In order to give a decisive proof that the compound is methylphenylsulphone, we prepared that substance synthetically, by the action of methyl iodide on sodium phenylsulphinate.

To an alcoholic solution of 8 grams (1 mol.) of phenylsulphinic acid and 8 grams (one mol.) of methyl iodide, an alcoholic solution of 1.3 grams of sodium was added, and the mixture heated at 100° , until no further separation of potassium iodide was noticed. The product evaporated to dryness on a water-bath, treated with water and the residue crystallised from alcohol yielded methylphenylsulphone, melting at 88° , with all the properties of the compound obtained from methylene-iodophenylsulphone:



It seemed possible that the replacement of the iodine of $\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{I}$ by organic radicals could be accomplished if the reactions took place at a lower temperature than is possible when using sodium phenylsulphinate, and, with this in view, we examined the action of ethyl, methyl and phenylsodium oxides on the iodo-sulphone.

With ethylsodiumoxide the reaction took place at 100° . An alcoholic solution of 0.45 gram (1 mol.) of sodium and 5 grams (1 mol.) of $\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{I}$ was heated in a flask, with reverse cooler, on a water-bath until the solution showed a neutral reaction. The contents of the flask were evaporated to dryness, water added to the residue and the insoluble substance crystallised from alcohol.

The substance obtained in this manner melted at 88° , and showed all the other properties of methylphenylsulphone.

The following analysis affords further proof:

0.2355 gram of substance gave 0.1109 gram of H_2O and 0.4979 gram of CO_2 .

	Theory for $C_6H_5SO_2CH_3$.	Found.
C	53.8	53.2
H	5.1	5.1

A similar experiment using methylsodiumoxide was next tried. Four grams of $C_6H_5SO_2CH_2I$, 0.3 gram of sodium were dissolved in absolute methyl alcohol, and the mixture heated at 100° until it became neutral. The contents of the flask, worked up as already described, gave methylphenylsulphone.

With sodiumphenyloxyde it was found necessary to heat in a sealed tube at a higher temperature, as no reaction took place in an open flask at 100° . Two grams (1 mol.) of $C_6H_5SO_2CH_2I$ and 0.9 gram (1 mol.) of C_6H_5ONa were dissolved in absolute alcohol, and the solution heated at 170° . This experiment gave methylphenylsulphone as the result of the reaction. We also made some experiments on the replacement of iodine of the iodo-sulphone by hydroxyl. Here we obtained an oil as the resulting product, which we shall make the subject of further investigation.

The reduction of an iodo-compound by the action of such substances as methyl or ethylsodium oxides is not without precedents, although, to our knowledge, the above-described reaction is the first certain instance of a mono-iodo-compound showing this property. We mention, as one of the few analogous reactions, the formation of methylene iodide by the action of ethylsodium oxide on iodoform.¹ The easy reducibility of iodine in both instances is obviously connected with the strong negative character of the iodo-compounds. It seems that the phenylsulphone group exercises a greater influence on the iodine atom than a second iodine, for we have obtained an oil which is undoubtedly methylene-oxyphenyl by the action of methylene iodide on phenylsodium oxide.

We wish, finally, to call attention to the fact of the formation of methylene-iodophenylsulphone, even though a large excess of sodium phenylsulphinat is used, as one of the most remarkable

¹ Butlerow, *Annalen*, **114**, 204. Schützenberger's chloro and iodo derivatives of acetic acid show similar properties, but the existence of these compounds seems doubtful.

instances of partial replacement of halogens, united with the same carbon atom, that is at present known in organic chemistry. It seems to us, irrespective of any hypothesis on the constitution of methylene iodide—and an explanation of the above fact is not likely to be given until an insight into intra-molecular dynamics is obtained—that a strict adhesion to facts permits of but one conclusion; and it is, that one of the iodine atoms of methylene iodide has a function different from the second; or, were it permissible to assume that the degree of replaceability be a measure of the force between the iodine and the carbon, then one of the iodine atoms of methylene iodide has a greater affinity for carbon than the other. H. Kolbe was the first to regard the difference in the behavior of the halogens of ethylene-halogen towards certain reagents, as proving a difference in the function of the halogens, but it is doubtful whether that eminent chemist would be willing to make the same assumption concerning the iodine of methylene iodide, since he regards the same hypothesis in regard to the chlorine of lead chloride as not justifiable, notwithstanding the formation of basic lead chloride by the action of ammonia on it.¹ There is, however, a notable difference between that reaction and the above-described, inasmuch as the basic lead chloride is insoluble, and for that reason, probably, less subject to the further action of the base, while in the latter reaction the iodo-compound remains in solution.

TUFTS COLLEGE, MASS., Oct. 11, 1884.

ON THE CONVERSION OF ORGANIC ISOCYANATES INTO MUSTARD OILS.

BY ARTHUR MICHAEL AND GEORGE M. PALMER.

Although the close relationship existing between oxygen and sulphur is characteristically shown in a large number of organic compounds containing these elements, in not a few instances a striking dissimilarity is noticed between the oxygen and the cor-

¹ Kurzes Lehrbuch der Chemie, 136.

responding sulphur compound. Thus the tendency to polymerisation, which the cyanate and isocyanate show so markedly, is only shown by the sulphocyanates at a high temperature and is apparently altogether lost in the mustard oils. Another example is found in the formation of metallic sulphocyanates by the addition of sulphur to cyanides, whereas the corresponding experiment with oxygen would have led to predict the formation of isosulphocyanates.

The question, Whether the replacement of the oxygen in the above-mentioned compounds would lead to the formation of corresponding sulphur derivatives? or, Whether there would be a splitting up into several molecules, accompanied by a molecular re-arrangement? seemed to present a field of considerable interest, and we publish the following preliminary work to reserve the right of future investigation in that direction. The replacement of oxygen by sulphur in organic compounds is dependent on the nature of the oxygen compound. In some compounds, like the aldehydes, the oxygen can be replaced by treatment with hydrogen sulphide; most oxygen compounds, however, are not acted on by that reagent. We are indebted to Kekule¹ for the introduction into organic chemistry of a reagent which possesses the power of replacing oxygen by sulphur in the great majority of oxygen compounds. Thus Kekule showed this to be true with anhydrides, Wislicenus² with acetones, Hofmann³ and Berntshen⁴ with amides.

The following experiments serve to prove that this is also the case with carbimides. Equal weights of phenylisocyanate and finely powdered phosphorus pentasulphide were heated, in a flask with reflux cooler, in an oil-bath at 160°. The disappearance of the sharp cyanate odor is noticeable after heating but a short time, and the reaction is entirely completed on heating the mixture several hours. The product of the reaction was heated with a free flame, as long as a liquid passed over, and the distillate subjected to fractional distillation. The greater part of the distillate passed over from 220°–225°, and a subsequent fractionation gave a liquid boiling between 222°–223°. This oil showed all the properties of phenyl mustard oil. Its formation was also proved by obtaining sulphocarbaniide by its action on aniline, and comparing the sub-

¹Annalen der Chemie **90**, 311.

³Berichte, 1878, 338.

²Zeitschrift für Chemie, 1869, 354.

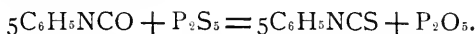
⁴Berichte, 1878, 503.

stance thus obtained with a product formed by the action of aniline on mustard oil,¹ as well as by a sulphur estimation.

0.2508 gram of substance gave 0.2617 gram of BaSO₄.

S	Theory for CS(NHC ₆ H ₅) ₂ .	Found.
	14.0	14.3

The yield of phenyl mustard oil obtained from phenylisocyanate by the action of P₂S₅ is almost the theoretical, and the reaction may be expressed as follows:



The formation of phenylisocyanate by the action of dehydrating agents on phenylurethane led us to expect, inasmuch as phosphorus pentasulphide possesses strong dehydrating properties, the direct formation of phenyl mustard oil by the action of the sulphide on the urethane. The result of our experiment confirmed our anticipation.

Ten grams of phenylurethane and 14 grams of phosphorus pentasulphide were mixed intimately, brought into a retort and heated in an oil bath. The oil which passed over was subjected to a fractional distillation, and consisted largely of a liquid boiling from 220°–225°. In a large measure this liquid was made up of phenyl mustard oil, but it was found impossible to separate it by distillation from a small quantity of ethyl mercaptane formed at the same time. To prove the presence of mustard oil, aniline was added, and the sulphocarbanilide thus obtained was found to be identical in its properties with the ordinary substance. The yield of mustard oil obtained by this method is satisfactory. We believe the method may be developed so as to be used to advantage in the preparation of mustard oils. It is hardly to be doubted that other urethanes would yield the corresponding mustard oils. From the distillate obtained by the action of P₂S₅ on phenylurethane, on standing for several weeks, a crystalline substance separated. This substance contained sulphur, but it is formed in so small a quantity that we were prevented from further examination.

In order to show that the formation of mustard oils from isocyanates is capable of generalisation, we prepared ethylisocyanate, by distilling potassium isocyanate with potassium ethylsulphate, and

¹ The melting point of sulphocarbanilide is given in text-books as 144°, although Bernthsen has, we believe, corrected it to 148°. The melting point of the compound we obtained was 153°, this we found to be correct for sulphocarbanilide prepared from phenyl mustard oil and aniline.

subjected it to the action of P_2S_5 . Five grams of ethylisocyanate and five of finely powdered P_2S_5 were heated, in a flask connected with a reversed cooler, until no liquid was noticed to condense in the cooler. The flask was heated as long as a liquid passed over, and the distillate subjected to a fractional distillation. The greater part of the oil passed over at 133° , and agreed perfectly in its other properties with those of ethyl mustard oil. It united with aniline to form ethylphenylsulphurea, melting at 99° .

A sulphur estimation gave the following result :

0.325 gram of CS $\left\{ \begin{array}{l} \text{NHC}_6\text{H}_5 \\ \text{NHC}_2\text{H}_5 \end{array} \right.$ gave 0.4246 gram of BaSO_4 .

	Theory for $\text{C}_9\text{H}_{12}\text{N}_2\text{S}$.	Found.
S	17.7	17.9

We have made several experiments in the direction indicated in the beginning of this note, and find that by the action of phosphorus pentasulphide on ethyl isocyanurate, a heavy oil; on methyl isocyanurate, a substance containing sulphur, and finally on potassium isocyanate, a crystalline body containing potassium and sulphur and easily soluble in alcohol, is formed. We hope to describe the results of these, and other similar experiments, in our next note on this subject.

TUFTS COLLEGE, MASS., Oct. 11, 1884.

INVESTIGATIONS ON THE SULPHINIDES.

BY IRA REMSEN.

The first representative of the class of compounds known as sulphinides was described by Fahlberg and myself,¹ who obtained it by oxidising ortho-toluene-sulphamide with potassium permanganate. While the isomeric amides of the meta- and para-series are converted by potassium permanganate into carboxyl acids of the formula $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{SO}_2\text{NH}_2 \\ \text{COOH} \end{smallmatrix}$, the product obtained from the

¹ This Journal **1**, 430.

ortho-amide contains the elements of water less than the normal acid. It is an anhydride of ortho-sulphamine-toluic acid, and, in accordance with the methods of representation generally adopted,

has one of the three formulas: $\text{C}_6\text{H}_4 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{CO} \end{array} \right\} > \text{NH}$, $\text{C}_6\text{H}_4 \left\{ \begin{array}{l} \text{SO}=\text{NH} \\ \text{CO} \end{array} \right\} > \text{O}$,

or $\text{C}_6\text{H}_4 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{C}=\text{NH} \end{array} \right\} > \text{O}$. Although we have no data enabling us

to decide positively between these three possibilities, we may for the present use the first and simplest expression. Since benzoic sulphinide was described, other bodies belonging to the same class have been discovered in this laboratory and elsewhere. Among them may be mentioned the following: The sulphinide,

$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2\text{NH}_2 \\ \text{SO}_2 \\ \text{CO} \end{array} \right\} > \text{NH}$, obtained by Fahlberg¹ by oxidising toluene-

disulphamide, $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2\text{NH}_2 \\ \text{SO}_2\text{NH}_2 \\ \text{CH}_3 \end{array} \right\} (m)$; mesitylenic sulphinide,

$\text{C}_6\text{H}_2 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{CO} \\ (\text{CH}_3)_2 \end{array} \right\} > \text{NH}$, obtained from mesitylene-sulphamide by Hall

and Remsen²; isophthalic sulphinide, $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{CO} \\ \text{CO}_2\text{H} \end{array} \right\} > \text{NH}$, described

by Remsen and Coale³ as a product of oxidation of sulphamine-metatoluic acid; terephthalic sulphinide, isomeric with the preceding compound and prepared by Remsen and Hall⁴ in the same way from sulphamine-paratoluic acid; and uvitic sulphinide,

$\text{C}_6\text{H}_2 \left\{ \begin{array}{l} \text{CO}_2\text{H} \\ \text{CO} \\ \text{SO}_2 \\ \text{CH}_3 \end{array} \right\} > \text{NH}$, obtained by Jacobsen⁵ from para-sulphamine-

mesitylenic acid.

The fact that ortho-toluene-sulphamide yields a sulphinide, while the corresponding meta- and para-amides do not, suggests, of course, that the ortho-relation of the carboxyl and sulphamine groups is the essential condition for the formation of the sulphinides. This is, further, in accordance with many other similar facts known to us regarding the formation of anhydrides, anhydro-

¹ This Journal **2**, 185.

² *Ibid.* **2**, 131.

³ *Ibid.* **3**, 209.

⁴ *Ibid.* **2**, 58.

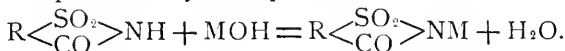
⁵ *Annalen der Chemie* **206**, 180.

bases, inner anhydrides, &c., and, although independent proof has not been furnished that in every sulphinide the characteristic groups do occupy the ortho-position relatively to each other, there is no reason to doubt that they actually occupy this position.

In a paper¹ on the oxidation of the sulphamides of naphthalene Comstock and Remsen have shown that the α -amide yields a sulphinide while the β -amide does not. As the oxidation of the α -amide can easily be effected and the product obtained in large quantity, the latter has been subjected to a thorough investigation, with the object of throwing as much light as possible upon the chemical character of the sulphinides. In the following paper an account is given of a number of derivatives of phthalic sulphinide, and experiments are described which show that, under some circumstances at least, possibly under all, the formation of salts of this compound is due to the replacement of the hydrogen of the imide group NH. It has hitherto been assumed that when any sulphinide, $R<\begin{smallmatrix} \text{CO} \\ \text{SO}_2 \end{smallmatrix}>\text{NH}$, yields a salt, the action takes place as represented by the general equation:



The product has been regarded as a salt of the corresponding sulphamine acid. The experiments to be described lead us, however, to the conclusion that probably the more common action should be represented by the equation:



Other sulphinides are now under investigation in this laboratory with particular reference to the character of their salts and esters, and it is hoped that it will be possible to determine the conditions which lead to the formation of salts in the sense of each of the above equations.

I.—ON PHTHALIC SULPHINIDE.

BY H. N. STOKES.

In the preparation of phthalic sulphinide the directions given by Comstock² were followed, though a few modifications were found to be advantageous. After some preliminary experiments, the following

¹ This Journal 5, 106.

² *Ibid.*

method was used: 40 grams amide and 32 grams potassium hydroxide were dissolved in water, and 180 grams potassium permanganate added in enough water to make the whole volume up to four litres. The oxidation began in the cold, and the solution became hot. It was finished by heating on a water-bath or over a free flame. When all the permanganate was reduced, which usually required from one to three hours, the mixture was filtered, hydrochloric acid added in excess to the filtrate, and the solution concentrated until crystallisation began. It is desirable not to add a large excess of acid at first, but this may safely be done when the crystallisation begins.

On cooling, the liquid was filled with fine needles of the salt, which was considered to be the acid potassium salt of sulphamine-phthalic acid. These were filtered off, boiled with strong alcohol recrystallised from water, again boiled with alcohol, and finally recrystallised from water, with addition of bone black. The object of boiling with alcohol was to remove phthalic acid and unoxidised amide. These were separated by converting the phthalic acid into the sodium salt and evaporating down to a small volume, when the amide crystallised out. In this way a small quantity of each of these substances was obtained. A further quantity of the acid potassium salt was obtained from the mother liquor by concentrating and separating from potassium chloride. Some sulphuric acid was also formed. Although considerable care was taken in working up the mother-liquors, nothing definite was obtained, except a small quantity of sulphophthalic acid which was isolated in the form of the barium salt. It is not certain that the sulphonic acid was formed during the oxidation process, for it was afterwards shown that it may be formed from the sulphamine acid by treatment with hydrochloric acid.

The crude acid salt, after standing for some time under water, was observed to be mixed with large transparent crystals. These were removed, recrystallised, and found to give the reactions of oxalic acid.

As products of the oxidation, therefore, we have chiefly phthalic sulphinide, obtained in the form of the potassium compound, a little phthalic, sulphuric and oxalic acids, with a small amount of undetermined products.

About 100 grams of pure acid potassium salt were obtained from 500 grams of the amide, which, as used, was not thoroughly

purified. The analyses of the potassium compound gave results like those already reported by Comstock.

0.2561 gram air-dried salt lost 0.0169 gram H_2O at 120° .

Calculated for		
$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 > \text{NK} + \text{H}_2\text{O}. \\ \text{CO} \\ \text{COOH} \end{array} \right.$		
H_2O	6.36	Found. 6.59

0.2265 gram anhydrous salt gave 0.0745 gram K_2SO_4 .

0.2392 gram anhydrous salt gave 0.0776 gram K_2SO_4 .

0.2135 gram anhydrous salt gave 0.1879 gram BaSO_4 .

0.2563 gram anhydrous salt gave 11.9 cc. N at 20° , and 770 mm.

Calculated for			
$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 > \text{NK}. \\ \text{CO} \\ \text{CO}_2\text{H} \end{array} \right.$			
		Found.	
K	14.72	14.75	14.54
S	12.08	12.08	...
N	5.28	5.36	...

The salt crystallises finely. It is very difficultly soluble in cold, but readily in hot, water. It is soluble in several hundred parts of boiling 95 per cent. alcohol, from which on cooling it separates in aggregations of small lance-shaped crystals. From water it crystallises according to circumstances. When precipitated by an acid from its solution in an alkali, it forms long needles, or delicate iridescent plates. In the latter form it comes down from its pure solution when rapidly cooled, but, if the clear solution is allowed to cool undisturbed, nothing comes down at first, but a slight jar starts the crystallisation, and then the size of the crystals seems to be limited only by the size of the vessel. Thus it was obtained in bunches of radiating, opaque, lustrous, lance-shaped crystals, some of which were from five to eight centimetres long. These, however, are very brittle, and readily break up into smaller ones. It loses water slowly but completely at 70° , and rapidly at 100° . It does not fuse below 250° , but does fuse at a much higher temperature.

Neutral potassium anhydro-sulphamine-phthalate,

$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 > \text{NK}. \\ \text{CO} \\ \text{COOK} \end{array} \right.$ The acid salt decomposes alkaline carbonates

readily, when slightly warmed with them. One molecular weight of the salt exactly neutralises one molecular weight of alkali, showing that the salt still contains one replaceable hydrogen. The

neutral potassium salt obtained by exact neutralisation with potassium carbonate, may be evaporated to a viscous mass without signs of crystallisation. After long standing, semi-crystalline, very soluble, globular masses made their appearance, probably indicating a slight tendency of the salt to crystallise. The salt is also easily soluble in alcohol. It may be heated to 300° , when it fuses without decomposition.

0.3296 gram dried at 170° gave 0.1878 gram K_2SO_4 .

0.2006 gram dried at 300° gave 0.1147 gram K_2SO_4 .

Calculated for		Calculated for	
$C_6H_3 \left\{ \begin{array}{l} SO_2 > NK \\ CO_2K. \end{array} \right.$		$C_6H_3 \left\{ \begin{array}{l} SO_2NH_2 \\ CO_2K. \end{array} \right.$	
Found.			
K	25.74	25.54 25.63	24.20

Potassium-ammonium anhydro-sulphamine-phthalate,

$C_6H_3 \left\{ \begin{array}{l} SO_2 > NK \\ CO_2NH_4 \end{array} \right.$. This is obtained by neutralising a solution of

the acid potassium salt with ammonia. On concentrating, ammonia is given off, and the solution becomes acid. The dissociation takes place but slowly, so that the solution may be evaporated to a syrup, which solidifies, on cooling, to a mass of crystals. The salt was not analysed.

Mono-silver anhydro-sulphamine-phthalate,

$C_6H_3 \left\{ \begin{array}{l} SO_2 > NAg \\ CO_2H \end{array} \right. + H_2O$. This is obtained by adding an ex-

cess of silver nitrate to a dilute boiling solution of the acid potassium salt. On cooling it crystallises out in fine, long, colorless, flexible needles, which are pure after one recrystallisation. Comstock also prepared this salt, but his statement that it does not lose water on heating is incorrect. It loses one molecule of water below 135° . It is not in the least discolored by light, and may be heated to 200° without decomposition. It is very difficultly soluble in cold, and by no means readily in hot, water. It may be recrystallised unchanged from dilute nitric acid.

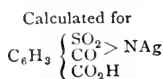
0.2474 gram air-dried salt lost 0.0141 gram H_2O at 135° .

0.1837 gram air-dried salt lost 0.0084 gram H_2O at 140° .

Calculated for		Found.	
$C_6H_3 \left\{ \begin{array}{l} SO_2 > NAg \\ CO_2H \end{array} \right. + H_2O$			
H_2O	5.11	5.70	5.47
20			

0.2333 gram anhydrous salt gave 0.0758 gram Ag.

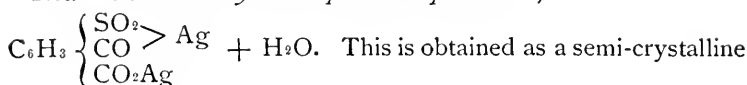
0.1753 gram anhydrous salt gave 0.0569 gram Ag.



Ag 32.34

Found.
 32.49 32.46

Neutral silver anhydro-sulphamine-phthalate,



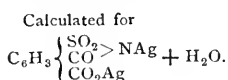
white precipitate on adding silver nitrate to a solution of the neutral potassium or potassium-ammonium salt. It is almost insoluble in boiling water. It is easily soluble in a boiling, moderately strong solution of potassium nitrate, from which it is deposited on cooling. Under some circumstances, however, this solution on cooling forms a transparent, moderately firm jelly. With nitric acid it gives the acid silver salt. It is not changed by light. It contains one molecule of water of crystallisation, which it loses below 135° , and even by long boiling under water. It cannot be heated above 165° without decomposing. The analyses do not agree well, as it cannot be purified by recrystallisation.

0.1858 gram air-dried salt lost 0.0069 gram H_2O at 135° .

0.1982 gram air-dried salt lost 0.0078 gram H_2O at 165° .

0.2026 gram air-dried salt lost 0.0079 gram H_2O at 160° .

0.1970 gram air-dried salt lost 0.0076 gram H_2O at 160° .



H_2O 3.92

Found.
 3.71 3.94 3.90 3.86

A portion of salt which had been boiled for a long time under water lost only a fraction of one per cent. of water at 160° .

I. 0.1904 gram anhydrous salt from the neutral potassium salt gave 0.0932 gram Ag.

II. 0.1894 gram anhydrous salt from the neutral potassium salt gave 0.0937 gram Ag.

III. 0.1947 gram anhydrous salt from the potassium ammonium salt gave 0.1251 gram $AgCl$.

IV. 0.2118 gram anhydrous salt from the potassium ammonium salt gave 0.1362 gram $AgCl$.

Calculated for		Found.		Calculated for
C_6H_3	$\left\{ \begin{array}{l} SO_2 > NAg. \\ CO_2 Ag \end{array} \right.$			C_6H_3
		I.	II.	$\left\{ \begin{array}{l} SO_2 NH_2 \\ CO_2 Ag \\ CO_2 Ag \end{array} \right.$
Ag	48.98	48.95	49.47	47.06
		III.	IV.	
		48.33	48.39	

The low results obtained in the last two analyses may be explained by the fact that the salt used was made from the potassium ammonium salt which had partly dissociated, thus giving a salt mixed with a little of the acid salt.

Neutral lead anhydro-sulphamine-phthalate,

$C_6H_3 \left\{ \begin{array}{l} SO_2 > N \\ CO > N \\ COO \end{array} \right. > Pb.$ An acid lead salt could not be prepared.

On mixing the acid potassium salt with lead acetate in the proportions of two molecular weights of the former to two of the latter, crystals of the neutral lead salt were obtained, mixed with unchanged potassium salt. The solution on evaporation gave off acetic acid. The same salt was obtained by mixing solutions of the neutral potassium salt and lead acetate.

The neutral lead salt crystallises in short, colorless, concentrically arranged prisms. It is almost insoluble in boiling water, and cannot be recrystallised. It contains one molecule of water of crystallisation, which it loses below 145° .

0.3102 gram air-dried salt lost 0.0137 gram H_2O at 160° .

0.2851 gram air-dried salt lost 0.0127 gram H_2O at 180° .

0.2869 gram air-dried salt lost 0.0115 gram H_2O at 170° .

0.2273 gram air-dried salt lost 0.0091 gram H_2O at 145° .

0.2181 gram air-dried salt lost 0.0102 gram H_2O at 200° .

Calculated for		Found.				
C_6H_3	$\left\{ \begin{array}{l} SO_2 > N \\ CO > N \\ COO \end{array} \right. > Pb + H_2O.$	I.	II.	III.	IV.	V.
H_2O	4.00	4.42	4.45	4.01	4.00	4.68

0.2965 gram anhydrous salt gave 0.206 gram $PbSO_4$.

0.2724 gram anhydrous salt gave 0.1872 gram $PbSO_4$.

0.2754 gram anhydrous salt gave 0.1874 gram $PbSO_4$.

0.2182 gram anhydrous salt gave 0.1474 gram $PbSO_4$.

0.2079 gram anhydrous salt gave 0.1462 gram $PbSO_4$.

Calculated for		Found.		Calculated for
C_6H_3	$\left\{ \begin{array}{l} SO_2 > N \\ CO > N \\ COO \end{array} \right. > Pb.$	I.	II.	C_6H_3
				$\left\{ \begin{array}{l} SO_2 NH_2 \\ CO_2 > Pb \\ CO_2 > Pb \end{array} \right.$
Pb	47.92	47.46	46.95	46.00
		IV.	V.	
		46.15	48.05	

With the exception of the last, the results lie between that required for a normal, and that for an anhydro-compound. The explanation may be that in the first four preparations which were made from acid potassium salt, a small quantity of an acid lead salt may have been contained. This is confirmed by the fact, that the fifth, which was made from neutral potassium salt, has the composition required by the anhydro formula. The formation of an ester,

$C_6H_3 \left\{ \begin{array}{l} SO_2 \\ CO \end{array} \right\} > NCH_3$, from the lead salt shows conclusively that it is an anhydro-compound.

Neutral barium salt. The acid potassium salt gives no precipitate with barium chloride, even after boiling or long standing. The neutral barium salt, obtained by boiling finely powdered and suspended barium carbonate with excess of the free acid, is almost insoluble in water. The results of an analysis were not satisfactory. The salt dried at 135° gave the following:

	Calculated for		Calculated for
	$C_6H_3 \left\{ \begin{array}{l} SO_2 \\ CO \end{array} \right\} > N > Ba.$	Found.	$C_6H_3 \left\{ \begin{array}{l} SO_2NH_2 \\ CO_2 \end{array} \right\} > Ba.$
Ba	37.85	36.36	36.05

Although this approaches much more nearly to the normal compound than that of the anhydro-compound, it appears, in view of the results reached in connection with the other salts, more probable that the salt analysed was not pure.

Anhydro-sulphamine-phthalic acid, or phthalic sulphinide,

$C_6H_3 \left\{ \begin{array}{l} SO_2 \\ CO \end{array} \right\} > NH + 2H_2O$. The free acid may be obtained by

decomposing the acid potassium salt with hot concentrated hydrochloric acid, but better by decomposing a hot solution of the acid silver salt with hydrochloric acid. On concentrating and allowing to cool, the free acid separates out, and may be obtained pure by one re-crystallisation. It is moderately soluble in cold, readily in hot water and in alcohol, but it is almost insoluble in ether. It crystallises from a moderately dilute aqueous solution in the form of short, thick, colorless needles, often concentrically grouped. From a hot concentrated solution it crystallises in spherical tufts of fine needles. When dry it has a pearly lustre. It contains two molecules of water of crystallisation, and loses one at 120° , and the

other at 155° , when its composition agrees with the formula, $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 > \text{NH} \\ \text{CO} > \text{NH} \\ \text{COOH} \end{array} \right.$. The fusing point of the crystallised acid as

observed in the capillary tube is not constant, but depends upon the size of the crystals and rapidity of heating. In general it is at about 155° – 160° , but is lower when the heating is rapid, and higher when it is very slow. It is accompanied with frothing from escape of water. The anhydride formed by heating for some time at 150° – 155° begins to sublime below 200° , but does not fuse even at 240° . If heated much higher, it fuses and sublims without apparent decomposition.

0.2329 gram air-dried acid lost 0.0165 gram H_2O at 120° , and 0.0152 gram H_2O at 155° .

0.2034 gram air-dried acid lost 0.0144 gram H_2O at 120° , and 0.0134 gram H_2O at 155° .

0.2288 gram air-dried acid gave 0.2034 gram BaSO_4 .

0.2657 gram air-dried acid gave 11.58 cc. N at 6.3° and 771 mm.

	Calculated for	Found.	
	$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 > \text{NH} \\ \text{CO} > \text{NH} \\ \text{COOH} \end{array} \right. + 2\text{H}_2\text{O}$		
1 H_2O	6.84	7.08	7.08
2 H_2O	13.69	13.61	13.67
S	12.17	12.19	...
N	5.32	5.38	...

That the water lost by heating is water of crystallisation and not of constitution, and that the anhydride is $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 > \text{NH} \\ \text{CO} > \text{NH} \\ \text{COOH} \end{array} \right.$ and

not $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO}_2\text{NH}_2 \\ \text{CO} > \text{O} \end{array} \right.$ will be shown farther on.

Mono-methyl anhydro-sulphamine-phthalate, $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 > \text{NCH}_3 \\ \text{CO} > \text{NCH}_3 \\ \text{COOH} \end{array} \right.$

Methyl iodide acts on the anhydrous acid silver salt even in the cold, the reaction being accompanied by a considerable evolution of heat. In a closed vessel the reaction is complete after heating half an hour at 100° . The product was extracted with alcohol, in which it is readily soluble, and purified by many recrystallisations from water. Two substances were isolated, the monomethyl ester

and a small quantity of a substance which crystallised from several hundred times its weight of boiling water in the form of delicate colorless curved needles, which fused at 156° . The quantity obtained was not sufficient for analysis, but it was evidently not the dimethyl ester described below, as they differ markedly in crystalline form and fusing point. The other substance proved to be the expected ester. It is readily soluble in cold alcohol, moderately soluble in cold, readily in hot, water. It crystallises in a number of forms. Occasionally it comes out of its solution in alcohol or water (when allowed to evaporate) in the form of long transversely striated prisms; at other times as tufts of delicate white needles one or two centimetres long, but usually as groups of concentric, long, narrow plates. After many recrystallisations it fuses constantly at 186° – 187° (uncorrected) or 190.7° – 191.7° (corrected). It is markedly volatile much below this temperature. When fused, it solidifies to a vitreous mass on cooling.

0.2045 gram air-dried substance gave 0.1972 gram BaSO_4 .

0.2226 gram air-dried substance gave 11.7 cc. N at 14.5° and 7.57 mm.

	Calculated for $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 > \text{NCH}_3 \\ \text{CO} \\ \text{COOH} \end{array} \right.$	Found.	Calculated for $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2\text{NH}_2 \\ \text{COOH} \\ \text{COOCH}_3 \end{array} \right.$
S	13.28	13.25	12.36
N	5.81	6.15	5.41

As the analyses of the neutral potassium, silver and lead salts were not decisive as to whether they are to be regarded as normal salts in which the two hydrogen atoms of the carboxyls are replaced by metals, or as compounds in which a carboxyl hydrogen and an imide hydrogen are replaced, it seemed possible that a study of the esters derived from the neutral silver and lead salts would throw some light on this subject, for it was to be assumed that they would more readily admit of purification than the salts themselves.

Dimethyl anhydro-sulphamine-phthalate, $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 > \text{NCH}_3 \\ \text{CO} \\ \text{COOCH}_3 \end{array} \right.$

This was prepared in three ways: 1st, from the neutral silver salt; 2d, from the neutral lead salt; 3d, from the monomethyl ester by treating with phosphorus pentachloride and methyl alcohol. The same substance was obtained in all cases.

Anhydrous neutral silver salt was heated with methyl iodide to 100° . The reaction was complete in half an hour. The product

was extracted with boiling alcohol in which it is but slightly soluble. On cooling there separated a mass of fine colorless needles. These were recrystallised from alcohol, and from a large quantity of boiling water, and proved on analysis to be the expected dimethyl ester.

0.1580 gram gave 0.1459 gram BaSO_4 .

0.2005 gram gave 0.1803 gram BaSO_4 .

0.1696 gram gave 0.1568 gram BaSO_4 .

0.2221 gram gave 10.99 cc. N at 21° and 757 mm.

Calculated for		Found.		C ₆ H ₃ { SO ₂ NH ₂ COOCH ₃ COOCH ₃ .	
C ₆ H ₃ { SO ₂ >NCH ₃ CO COOCH ₃ .					
N	5.49	5.61		5.13	
S	12.55	12.66	12.37	12.60	11.72

As every precaution was taken to purify the substance, and the fusing point did not change after many crystallisations, the figures leave no doubt as to the formula to be selected. This ester, as well as the salts from which it was made, is derived from the sulphinide by the replacement of the imide hydrogen and a carboxyl hydrogen. The dimethyl ester fuses at 176° (uncorrected) and 180° (corrected). It is difficultly soluble in cold, and very moderately soluble in hot, methyl and ethyl alcohol. It dissolves in not less than 10,000 parts of cold water, and not less than 500 parts of boiling water. From its hot aqueous or alcoholic solution it crystallises in slender, colorless, brittle needles, often as long as three centimetres. It volatilises perceptibly even at 120° . Heated above its fusing point it readily sublimes without decomposition, forming delicate iridescent plates melting at 176° (uncorrected). The fused mass crystallises in long prisms on cooling.

In making the ester from the neutral lead salt it is necessary to heat with methyl iodide in a sealed tube to 120° . The product is identical with that obtained from the silver salt.

Now, as the neutral silver salt and the neutral lead salt used in making the ester were themselves made from the neutral potassium salt, and, as the ester is thus shown to have the formula

$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 > \text{NCH}_3 \\ \text{CO} \\ \text{CO}_2\text{CH}_3 \end{array} \right.$ and not $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2\text{NH}_2 \\ \text{CO}_2\text{CH}_3 \\ \text{CO}_2\text{CH}_3 \end{array} \right.$, it appears highly

probable that the salts themselves have the formulas already ascribed to them, and deduced from the results obtained in analysing them.

They are constituted according to the formula, $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{CO} \\ \text{CO}_2\text{M} \end{array} \right\} > \text{NM}$
 and not $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2\text{NH}_2 \\ \text{CO}_2\text{M} \\ \text{CO}_2\text{M} \end{array} \right\}$.

When a solution of phthalic sulphinide is neutralised salts of the above order are obtained, at least in the cases studied. From this it follows that in solution phthalic sulphinide retains the anhydride condition, and that the water given off from the crystallised substance is water of crystallisation and not water of constitution. It is correctly represented by the formula,

$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{CO} \\ \text{CO}_2\text{H} \end{array} \right\} > \text{NH} + \text{H}_2\text{O}$, for plainly if it corresponded to the

formula $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2\text{NH}_2 \\ \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{array} \right\}$, the neutral salts would correspond to the

second of the above formulas.

It is not at all surprising that the imide hydrogen contained in the sulphinide ring $\text{—CO—SO}_2 > \text{NH}$ should have acid properties.

Many facts are known which would lead us to expect these properties. In the first place, in many of the primary amides the amide hydrogen may be in part replaced by a metal. Thus, for example, acetamide, CH_3CONH_2 , gives the compounds CH_3CONHAg , $(\text{CH}_3\text{CONH})_2\text{Hg}$ and $(\text{CH}_3\text{CONH})_2\text{Zn}$, and many other examples might be quoted. The sulphamides have the same property. Thus we have from benzene-sulphamide the salt $\text{C}_6\text{H}_5\text{SO}_2\text{NHAg}$, and from α -naphthalene-sulphamide, $\alpha\text{C}_{10}\text{H}_7\text{SO}_2\text{NHAg}$. The replacement of one hydrogen in the amide group by an acid radical gives still more strongly acid properties to the remaining hydrogen atom. Thus in dibenzamide,

$\text{C}_6\text{H}_5\text{CO} > \text{NH}$, the imide hydrogen may readily be replaced by

sodium¹ by dissolving in caustic soda, and from the sodium salt others may be prepared. A still stronger acid is obtained when the compound has the formula $\text{R.SO}_2 > \text{NH}$ in which R and R'

¹ Barth and Senhofer, *Berichte der deutschen chemischen Gesellschaft* 9, 976.

represent the same or different aromatic radicals. Thus Gerhardt and Chiozza¹ obtained benzoyl-benzene-sulphamide,

$\text{C}_6\text{H}_5\cdot\text{CO}$
 $\text{C}_6\text{H}_5\cdot\text{SO}_2 > \text{NH}$, and showed that it has acid properties. Other

similar compounds have since been made.² While the salts of compounds of the general formula $\text{R}\cdot\text{SO}_2\text{NH}_2$ are very unstable, being even decomposed by carbon dioxide,³ the compounds of the

order $\frac{\text{R}\cdot\text{SO}_2}{\text{R}\cdot\text{CO}} > \text{NH}$ are strong acids, readily decompose carbonates and form stable salts. The characteristic group of these acids is

$\frac{\text{SO}_2}{\text{CO}} > \text{NH}$. Now, in the sulphinides, we have instead of a com-

pound $\frac{\text{R}'\cdot\text{SO}_2}{\text{R}'\cdot\text{CO}} > \text{NH}$, one of the formula $\text{R}'' < \frac{\text{SO}_2}{\text{CO}} > \text{NH}$. It is

difficult to see why a substance of the latter constitution should not be as strong an acid as one of the former, and give salts in which the metal replaces the imide hydrogen. As has been shown above, such is certainly the case with phthalic sulphinide. Only one other undoubted case has previously been described. It is that of mesitylenic sulphinide, of which a silver salt of the for-

mula $\text{C}_6\text{H}_2 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{CO} \end{array} \right\} > \text{NAg}$ has been described by Remsen and Hall.⁴

Constitution of the Acid Salts.

An interesting question suggests itself regarding the constitution of the acid salts of phthalic sulphinide. Are these salts

properly represented by the formula, $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{CO} \\ \text{CO}_2\text{M} \end{array} \right\} > \text{NH}$, or by

$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{CO} \\ \text{CO}_2\text{H} \end{array} \right\} > \text{NM}$? In other words, does the metal replace the

hydrogen of the carboxyl, or that of the imide group?

The simplest way to decide the question seemed to be to study the action of phosphorus pentachloride and an alcohol on the acid potassium salt.

According to Remsen and Fahlberg⁵ benzoic sulphinide is not acted upon by phosphorus pentachloride, even when heated with

¹ Jahresberichte der Chemie, 1856, 503.

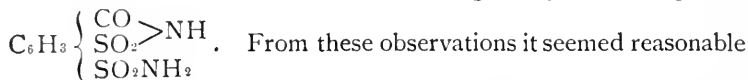
² Gerhardt and Chiozza, *loc. cit.*; Wolkow, Zeitschrift für Chemie, 1870, 579; 1871, 421.

³ *Loc. cit.*

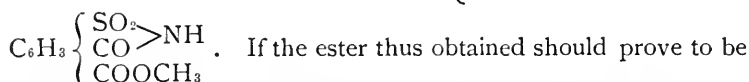
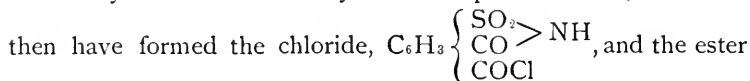
⁴ This Journal 2, 135.

⁵ *Ibid.* 1, 431.

it. The same statement is made¹ regarding the compound



to assume that the sulphinide ring in phthalic sulphinide would show a similar stability, while the carboxyl would almost certainly be attacked. By the successive action of phosphorus pentachloride and methyl alcohol on the anhydrous acid potassium salt, we should



identical with the monomethyl ester above described, which was formed from the acid silver salt, it would follow that in the latter ester, and hence probably in all members of the acid series to which it belongs, the radical or metal replaces the carboxyl hydrogen. If, on the other hand, the esters obtained by the two methods should prove to be isomeric, proof would thus be furnished that the radical or metal replaces the imide hydrogen.

Perfectly anhydrous acid potassium salt was finely mixed with two parts phosphorus pentachloride. The reaction took place rapidly on warming for a short time on the water-bath. An unsuccessful attempt was made to extract the chloride with anhydrous ether. The residue left after distilling off the ether from many extractions was solid, but, after washing with anhydrous ether to remove phosphorus oxychloride, it contained only three per cent. chlorine, while the calculated percentage of chlorine in the chloride is 14.46.

The extraction was effected by heating with phosphorus oxychloride containing a little ether. On cooling, the filtrate deposited small transparent prisms. These were well washed with anhydrous ether, pressed between layers of bibulous paper and placed over sulphuric acid. It was not thought best to recrystallise the substance, and it was analysed directly. It fused at 120°–126°, and contained sulphur, chlorine, nitrogen and phosphorus.

0.1871 gram decomposed by boiling water gave 0.3151 gram AgCl.

0.2835 gram decomposed by boiling water gave 0.0700 gram $\text{Mg}_3\text{P}_2\text{O}_7$.

¹ This Journal 2, 186.

	Calculated for $C_6H_3 \left\{ \begin{array}{l} SO_2 \\ CCl_2 \\ COCl \end{array} \right\} > N \cdot POCl_2$	Found.
Cl	42.51	41.64
P	7.43	6.88

These results, while not satisfactory, agree more closely with the above than with any other formula. The presence of chlorine in place of the carboxyl oxygen is supported by analogy and by the formation of the trimethyl ester described below. The quantity of material did not suffice for another analysis, and a second attempt to obtain it in the crystalline form failed. The low percentage of chlorine may be explained by its having been decomposed slightly by the moisture of the air.

Phosphorus compounds similar to that just described have been obtained by Wallach. Thus he obtained¹ a compound $CO_2C_2H_5$

$|$
 $CCl_2 \cdot NHPOCl_2$ by treating oxamethane with phosphorus pentachloride, and in the same way the compound $CHCl_2 \cdot CCl_2 \cdot N(C_2H_5) \cdot POCl_2$ was made from the ethyl-amide of dichloroacetic acid, $CHCl_2 \cdot CONHC_2H_5$.² Generally, it is true the first chlorides of the formula $R \cdot CCl_2 \cdot NHR$ lose hydrochloric acid and are converted into products of the formula $R \cdot CCl = NR$,³ and Gerhardt,⁴ Wallach⁵ and Wolkow⁶ have shown that when phosphorus pentachloride acts upon an amide of the formula $\begin{array}{l} R \cdot SO_2 \\ R \cdot CO \end{array} > NH$, a product of the formula $\begin{array}{l} R \cdot SO_2 \\ R \cdot CCl \end{array} \geq N$ is formed.

In view of the above facts it is not surprising that a compound $R'' \left\{ \begin{array}{l} SO_2 \\ CO \end{array} \right\} > NH$, such as phthalic sulphinide, should give a compound $R'' \left\{ \begin{array}{l} SO_2 \\ CCl_2 \end{array} \right\} > N \cdot POCl_2$, rather than $R'' \left\{ \begin{array}{l} SO_2 \\ CCl \end{array} \right\} \geq N$. That the product was not of the latter kind is shown conclusively by the analyses and by the formation of the trimethyl ester.

Trimethyl anhydro-sulphamine-phthalate,

$C_6H_3 \left\{ \begin{array}{l} SO_2 \\ C(OCH_3)_2 \\ COOCH_3 \end{array} \right\} > NH$. While it has not proved possible to

¹ *Annalen der Chemie* **184**, 7.

² *Ibid.* **214**, 223.

³ *Ibid.* **184**, 33, 79, 88; **214**, 202.

⁴ *Ibid.* **108**, 214.

⁵ *Ibid.* **214**, 210.

⁶ *Berichte der deutschen chemischen Gesellschaft* **5**, 139.

obtain salts of phthalic sulphinide which contain more than two atoms of a univalent metal, it is otherwise with the esters. Three methyl groups have been introduced, and the possibility of introducing a fourth is indicated. The liquid from which the chloride above mentioned had crystallised was mixed with an excess of methyl alcohol. A violent reaction took place, so that the liquid had to be kept cool. The excess of methyl alcohol was distilled off, leaving a syrup which crystallised on cooling. This syrup was dissolved in a little hot water, and the solution on cooling deposited abundant crystals. These were recrystallised several times from water when they had a constant fusing point. They contain no water of crystallisation and fuse without loss of weight, the fused mass forming a vitreous mass on cooling, which does not become crystalline after long standing.

0.2126 gram gave 0.1769 gram BaSO_4 .

0.2341 gram gave 9.95 cc. N at 19° and 761 mm.

0.2280 gram gave 10.45 cc. N at 23° and 762 mm.

	Calculated for	Found.
	$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{C}(\text{OCH}_3)_2 \\ \text{CO}_2\text{CH}_3 \end{array} \right\} > \text{NH}.$	
S	11.15	11.43
N	4.88	4.89 5.18

These results indicate that the substance is a trimethyl ester, as would be expected from a chloride of the above composition. The ester is easily soluble in cold alcohol, moderately soluble in cold, easily in hot water, from which it crystallises in groups of concentric long slender needles, or more frequently in groups of concentric long narrow plates. In appearance it can scarcely be distinguished from the monomethyl ester. It fuses at $140.5\text{--}141.5^\circ$ (uncorrected); $143.5\text{--}144.5^\circ$ (corrected).

To prove that this ester actually corresponds to the crystallised chloride, a small portion of the latter was treated with methyl alcohol. The product obtained had the same appearance and fused at the same point as the ester analysed.

The formation of the chloride, $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{CCl}_2 \\ \text{COCl} \end{array} \right\} > \text{NH}$, and the ester,

$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{C}(\text{OCH}_3)_2 \\ \text{CO}_2\text{CH}_3 \end{array} \right\} > \text{NH}$, is analogous to the formation of phthalyl chloride and the esters of phthalic acid recently described by Graebe.

This chemist has shown¹ that there are two dimethyl esters of phthalic acid, one formed by means of the silver salt and methyl iodide, the other from the chloride and sodium methylate. The former is probably to be represented by the formula $C_6H_4 \begin{Bmatrix} CO_2CH_3 \\ CO_2CH_3 \end{Bmatrix}$, and the latter by $C_6H_4 \begin{Bmatrix} CO \\ C(OCH_3)_2 \end{Bmatrix} > O$. Similarly tetrachlorophthalic acid gives two diethyl esters.

The trimethyl ester, $C_6H_3 \begin{Bmatrix} SO_2 \\ C(OCH_3)_2 \\ CO_2CH_3 \end{Bmatrix} > NH$, contains an imide hydrogen, which by analogy should be replaceable by methyl, thus giving a tetramethyl ester.

A hot solution of the ester was treated gradually with very dilute caustic soda. The solution was heated a few moments, when the slight excess of alkali disappeared. More alkali was added and the heating continued until the reaction became permanently alkaline. It was then precipitated with silver nitrate, the precipitate dried at 160° , and heated with methyl iodide. Instead of the expected tetramethyl ester, nothing was obtained but the dimethyl ester melting at 176° . Hence the alkali had saponified the ester, giving the free acid or the monomethyl ester, either of which treated as above would give the dimethyl ester. Lack of time and material prevented further attempt to obtain the tetramethyl ester.

As the experiments just described failed to accomplish the object for which they were undertaken, that is, the determination of the constitution of the acid salts of phthalic sulphinide, the study of the action of phosphorus pentachloride and methyl alcohol on the monomethyl ester was undertaken with the same object in view.

It has been found that phosphorus pentachloride does not readily act on carboxyl when its hydrogen is replaced by an alcohol radical. Hence we should expect the following results, depending upon the constitution of the monomethyl ester.

I. If it has the constitution, $C_6H_3 \begin{Bmatrix} SO_2 \\ CO > NH \\ COOCH_3 \end{Bmatrix}$, we would probably have formed the chloride, $C_6H_3 \begin{Bmatrix} SO_2 \\ CCl_2 > NH \\ COOCH_3 \end{Bmatrix}$, and the ester,

¹ Berichte der deutschen chemischen Gesellschaft **16**, 860.

$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{C}(\text{OCH}_3)_2 \\ \text{COOCH}_3 \end{array} \right\} > \text{NH}$, *i. e.* the trimethyl ester above described.

II. If, on the other hand, the monomethyl ester has the constitution $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{CO} \\ \text{CO}_2\text{H} \end{array} \right\} > \text{NCH}_3$, we would have either the pro-

ducts corresponding to the formulas, $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{CO} \\ \text{COCl} \end{array} \right\} > \text{NCH}_3$ and

$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{C}(\text{OCH}_3)_2 \\ \text{COOCH}_3 \end{array} \right\} > \text{NCH}_3$, or the product $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{CO} \\ \text{COCl} \end{array} \right\} > \text{NCH}_3$

and $\left\{ \begin{array}{l} \text{SO}_2 \\ \text{CO} \\ \text{COOCH}_3 \end{array} \right\} > \text{NCH}_3$, *i. e.* either a tetramethyl ester or a dimethyl

ester identical with that already described, and obtained from the neutral lead and silver salts.

Some of the monomethyl ester was intimately mixed with two parts of phosphorus pentachloride. The reaction took place but slowly even on the water-bath. A small portion of the product gave with water the original ester melting at 186° – 187° . This chloride resists the action of water much more strongly than the crystallised chloride above described, and has to be boiled for some time before it is completely decomposed. The remainder of the product was boiled with an excess of methyl alcohol. An ester was thus obtained which after recrystallisation from water fused at 174° (uncorrected), and in every other respect resembled the dimethyl ester $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{CO} \\ \text{CO}_2\text{CH}_3 \end{array} \right\} > \text{NCH}_3$. The reaction appeared to be quantitative.

Hence, according to the above considerations, the only possible formula for the monomethyl ester is $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 \\ \text{CO} \\ \text{COOH} \end{array} \right\} > \text{NCH}_3$, and,

since this is derived by simple transformations from the acid potassium salt, it follows that in the acid series it is the imide hydrogen which is replaced by the metal or radical, and that in phthalic sulphinide the imide hydrogen has stronger acid properties than that of the carboxyl.

Finally, perfectly anhydrous phthalic sulphinide was treated successively with phosphorus pentachloride and methyl alcohol

and the same trimethyl ester was obtained as from the acid potassium salt by similar treatment. As this ester has been shown to correspond to the formula $C_6H_3 \left\{ \begin{array}{l} SO_2 \\ C(OCH_3)_2 \\ COOCH_3 \end{array} \right\} > NH$, it follows that

of the two possible formulas for the free acid, viz. $C_6H_3 \left\{ \begin{array}{l} SO_2 \\ CO \\ CO_2H \end{array} \right\} > NH$

and $C_6H_3 \left\{ \begin{array}{l} SO_2NH_2 \\ CO \\ CO > O \end{array} \right\}$, the former is the correct one, for, in case the compounds were constituted according to the second formula, the product obtained would in all probability be a dimethyl ester



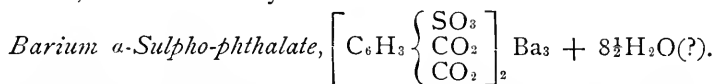
It will be observed that when phosphorus pentachloride acts on the free acid or its salts, the sulphinide ring is attacked, but that

when it acts on the ester, $C_6H_3 \left\{ \begin{array}{l} SO_2 \\ CO \\ CO_2H \end{array} \right\} > NCH_3$, the ring remains intact.

α-Sulpho-phthalic Acid.

Phthalic sulphinide is slowly attacked by concentrated hydrochloric acid at 100°, but by heating to 150° it is rapidly and completely changed into sulphophthalic acid. Some of the acid potassium salt was thus treated, and the product evaporated to dryness to expel hydrochloric acid. It was then dissolved in a little hot water. No phthalic acid or phthalic sulphinide separated on cooling. The solution was diluted with a large quantity of water, and boiled with an excess of barium carbonate. The barium salt which separated from the filtrate on cooling was recrystallised from

water, and exactly resembled the salt $\left[C_6H_3 \left\{ \begin{array}{l} SO_3 \\ CO_2 \\ CO_2 \end{array} \right\} \right] Ba_3$ otherwise obtained, and described by Comstock.¹



The salt loses part of its water at a low temperature, so that though stable in the air, it cannot be obtained with exactly the same per-

¹ This Journal 5, 107.

centage of water in any two cases. It loses most of its water at 100° , and about one molecule between this and 250° , but no very concordant results could be obtained. After drying at 100° it is very hygroscopic, and in a few hours will take up nearly as much water as it has lost.

The following analyses were made of a salt crystallised from very dilute solutions, so that the liquid had time to cool considerably before crystallisation began:

0.2688 gram air-dried salt lost 0.0396 gram H_2O at 285° .

0.2070 gram air-dried salt lost 0.0309 gram H_2O at 285° .

Calculated for		Found.	
$\left[\text{C}_6\text{H}_3 \left\{ \begin{smallmatrix} \text{SO}_3 \\ \text{CO}_2 \\ \text{CO}_2 \end{smallmatrix} \right\}_2 \right] \text{Ba}_3 + 8\frac{1}{2}\text{H}_2\text{O}.$			
H_2O	14.57	14.73	14.93

Other preparations crystallised at a higher temperature gave a considerably lower percentage of water.

0.2292 gram salt dried at 285° gave 0.1770 gram BaSO_4 .

0.1761 gram salt dried at 285° gave 0.1371 gram BaSO_4 .

Calculated for		Found.	
$\left[\text{C}_6\text{H}_3 \left\{ \begin{smallmatrix} \text{SO}_3 \\ \text{CO}_2 \\ \text{CO}_2 \end{smallmatrix} \right\}_2 \right] \text{Ba}_3.$			
Ba	45.83	45.42	45.77

The salt gives a fine green fluorescence when heated with resorcin and sulphuric acid and dissolved in an alkali. No acid salt could be obtained by treating with hydrochloric acid.

Neutral potassium α -sulpho-phthalate, $\text{C}_6\text{H}_3 \left\{ \begin{smallmatrix} \text{SO}_3\text{K} \\ \text{CO}_2\text{K} \\ \text{CO}_2\text{K} \end{smallmatrix} \right.$ This is

obtained by treating a hot solution of the barium salt with potassium carbonate. It is extremely soluble in water, and could not be obtained in crystalline form. No crystallised acid salt could be obtained by treating the concentrated solution with hydrochloric acid.

Mono-potassium di-silver α -sulpho-phthalate,

$\text{C}_6\text{H}_3 \left\{ \begin{smallmatrix} \text{SO}_3\text{K} \\ \text{CO}_2\text{Ag} \\ \text{CO}_2\text{Ag} \end{smallmatrix} \right. + 2\text{H}_2\text{O}.$ If a solution of silver nitrate is added to

a hot and sufficiently dilute solution of the neutral barium or potassium salt, a clear solution is obtained, which solidifies to a transparent jelly on cooling. One part of salt in several hundred parts of water will form a jelly so firm that the vessel may be inverted without losing the contents.

The neutral potassium salt in moderately concentrated solution gives with silver nitrate a heavy precipitate which is almost insoluble in boiling water, but which dissolves quite readily in a hot moderately dilute solution of potassium nitrate. This solution may also gelatinise, but ordinarily it deposits iridescent scales on cooling. If to a very dilute solution of the potassium salt a solution of silver nitrate is added drop by drop, masses of perfectly transparent jelly are formed, which fall to the bottom or remain hanging from the surface of the liquid or sides of the vessel. In a few minutes these become slightly opaque, and this is seen to be owing to the formation of small scales on the surface. These drop off and are replaced by others, so that in an hour the jelly has become converted into scales. For all these cases the salt formed contains one atom of potassium to two of silver, and two molecules of water of crystallisation. It loses this water at 100° , and is then quite hygroscopic.

0.2063 gram air-dried salt lost 0.0134 gram water at 105° .

0.2008 gram air-dried salt lost 0.0126 gram water at 140° .

Calculated for		Found.	
$C_6H_3 \left\{ \begin{array}{l} SO_3K \\ CO_2Ag \\ CO_2Ag \end{array} \right. + 2H_2O$			
$2H_2O$	6.74	6.49	6.27

0.1882 gram anhydrous salt dissolved in nitric acid gave 0.1079 gram $AgCl$. The filtrate evaporated to dryness gave 0.0343 gram K_2SO_4 .

Calculated for		Found.	
$C_6H_3 \left\{ \begin{array}{l} SO_3K \\ CO_2Ag \\ CO_2Ag \end{array} \right.$			
Ag_2	43.37	43.15	
K	7.83	8.18	

With lead acetate the neutral potassium salt gives a gelatinous precipitate which is difficultly soluble in boiling water, the solution gelatinising imperfectly on cooling. It could not be obtained in crystalline form. It is easily soluble in a hot solution of potassium nitrate, and comes down as an amorphous mass on cooling.

0.2309 gram dried at 175° gave 0.1741 gram $PbSO_4$.

The filtrate gave 0.0195 gram K_2SO_4 .

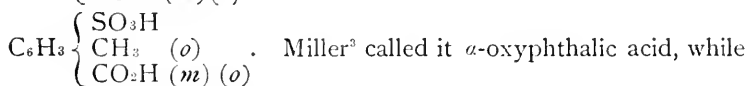
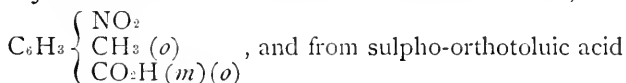
Calculated for		Found.		Calculated for	
$C_6H_3 \left\{ \begin{array}{l} SO_3 \\ CO_2 \\ CO_2 \end{array} \right\} Pb_2$				$C_6H_3 \left\{ \begin{array}{l} SO_3K \\ CO_2 \\ CO_2 > Pb \end{array} \right.$	
Pb	56.10	51.49			42.33
K	...	3.77			7.98

Hence the salt is probably impure neutral lead salt. The potassium found probably came from the mother liquors which could not be completely removed by washing or pressing.

α -Oxyphthalic Acid.

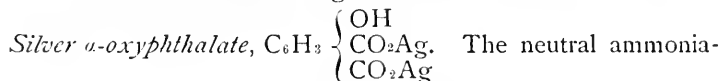
This acid was first obtained by Miller¹ from α -amidophthalic acid made from the nitrophthalic acid of melting point 212° , and also by oxidising acetyl- α -naphthol with chromic acid.

Jacobsen² obtained it from nitro-orthotoluic acid,



Jacobsen called it β -oxyphthalic acid. It is characterised by giving a deep cherry-red color with ferric chloride, while the isomeric acid gives a reddish yellow. If the acid has the formula ascribed to it, it should be obtained by fusing phthalic sulphinide with caustic potash. The acid potassium salt was fused with caustic potash and a little water. The product was acidified and extracted with ether. The substance thus obtained gave an intense cherry-red color with ferric chloride. When dilute it has a more purple tint, but cannot be confused with that produced by salicylic acid. To purify the acid the dry ethereal extract was dissolved in a little ether and precipitated by petroleum benzine. The crystals thus obtained fused at 145° – 150° with frothing from escape of water. According to Jacobsen¹ the acid fuses at 200° when rapidly heated, but much lower, with formation of anhydride, when slowly heated. The anhydride melts at 145° – 148° . The acid decomposes to a great extent when sublimed, but the sublimate still gives a cherry-red color with ferric chloride.

The *neutral ammonium salt* gives off ammonia when boiled.



cal solution of the acid gives a white precipitate with silver nitrate. This is difficultly soluble in boiling water. When well washed it

¹ Annalen der Chemie **208**, 247.

² Berichte der deutschen chemischen Gesellschaft **16**, 1965.

³ *Ibid.* **17**, 552.

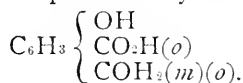
⁴ *Ibid.* **16**, 1965.

is not sensitive to light and does not decompose very readily on heating, as stated by Miller.¹ It contains no water of crystallization.

0.2044 gram dried at 110° gave 0.1121 gram Ag.

	Calculated for $C_6H_3(OH)(CO_2Ag)_2$.	Found.
Ag	54.54	54.84

Hence the substance is the α -oxyphthalic acid of Miller. Its formation from α -nitronaphthalene, on the one hand, and from α -naphthalene-sulphonic acid on the other, establishes a line of connection between these two derivatives of naphthalene; and if it be assumed, as seems justifiable, that the formation of the sulphide is dependent upon the ortho-relation between a sulphamide group and carboxyl, it follows that in α -nitronaphthalene the nitro group is situated in the ortho position relatively to one of the carbon atoms common to both benzene residues; and that the constitution of α -oxyphthalic acid is represented by the formula



NOTES.

On the Permeability of Silver for Oxygen Gas.

Some years ago Sainte-Claire Deville and Troost showed that hydrogen gas is capable of passing through platinum and iron at a red heat. Recently the latter of these investigators has shown that silver acts in a similar way towards oxygen.

A tube of pure silver of 0.01 m. diameter and with walls 0.001 m. thick was enclosed in a somewhat larger platinum cylinder, and the whole heated in the vapor of boiling cadmium. On exhausting the silver tube with a Sprengel pump, and passing oxygen into the space around it, the gas was found to enter at a rate corresponding to 1.700 lit. per hour for each square meter of surface exposed. On passing air instead of oxygen into the outer chamber, oxygen with only a trace of nitrogen was found in the interior, but the rate of transfusion was diminished nearly one-half. By using a tube of slightly thinner walls, the gas entered much more rapidly. Instead of exhausting the tube, the author found it necessary only to pass slowly through it a stream of some other gas, such as carbon

¹ *Annalen der Chemie* **208**, 247.

dioxide; although this lessened considerably the rate of trans-
fusion. The oxygen was replaced by other gases, such as carbon
dioxide, carbon monoxide, and nitrogen, but they passed through
the walls of the tube with extreme slowness. The author states in
conclusion that this property of silver may some time be utilised to
extract oxygen directly from the atmosphere. For this purpose
it would be necessary to expose a large surface by using coils of
tubes with thin walls; and to use either an exhaust pump, or a
stream of carbon dioxide, which could be absorbed by an alkali,
leaving pure oxygen.—(*Compt. Rend. de l'Acad.* 98, 1427.)

J. R. D.

Recent Methods for the Preparation of Aluminium.

H. A. Gadsden,¹ of London, has patented a process for the
manufacture of aluminium, the new feature of which consists in
bringing the aluminium chloride and metallic sodium together in
the form of vapors. Corundum or bauxite is mixed with about
ten per cent. of fluoride of sodium or potassium and the mixture
calcined on the hearth of a roasting furnace. After the roasted
mass has been pulverised, ten per cent. of charcoal is added, and
after thorough mixing and calcining, the mixture is introduced into
a retort and heated to a high temperature. A current of chlorine
is passed into the retort and the aluminium chloride formed distills
over and may be condensed.

For the reduction of the aluminium chloride a furnace is provided
in which two earthenware retorts are connected with each other.
In one of these aluminium chloride is volatilised, in the other an
intimate mixture of sodium carbonate, charcoal and calcium car-
bonate is heated to a high temperature. The vapors of metallic
sodium thus formed pass over into the first retort, the aluminium
chloride is decomposed, the metallic aluminium being deposited
as a powder in the bottom of the retort, from whence it is easily
removed and cast into bars.

W. Weldon² proposes to obtain aluminium by fusing cryolite
with calcium chloride, or some other non-metallic chloride or
sulphide, and to reduce the aluminium chloride or sulphide with
metallic manganese.

H. Miwerth³ mixes ferrosilicon with aluminium fluoride in mole-
cular proportions and heats the mixture to fusion. Double
decomposition takes place, silicon fluoride is formed which
volatilises, and an alloy of iron and aluminium remains. Alum-
inium bronze may be obtained directly by fusing the iron alum-
inium alloy with copper. The aluminium unites with the copper
and the iron remains with but a very small quantity of aluminium.
Pure aluminium is obtained by heating aluminium chloride with
silicon.

E. H. K.

¹ Dingler's Polytechnisches Journal 253, 426.

² *Ibid.* 252, 515.

³ *Ibid.* 252, 515.

Examination of Fats and Oils.

Hübl¹ describes a systematic method for the detection of fats and oils. It is based upon the fact that nearly all fats are composed of the glycerin ethers of members of three groups of fatty acids. These are the acetic, acrylic and tetrolic acid series. The relative proportion of these acids in any variety of fat or oil is constant within certain limits, and this proportion is different only in different kinds of oils. The members of the three groups of acids, however, exhibit a very different behavior towards chlorine, bromine and iodine, while under ordinary circumstances the acids of the first series are indifferent, those of the second and third series readily unite with definite quantities of the halogens and substitution products of the first series are formed.

If, therefore, it is possible to make a fat unite with a halogen under circumstances which preclude the possibility of substitution, and the amount which enters into the compound be accurately determined, the number thus obtained would be a constant, and would be dependent upon the amount of unsaturated acids present in the fat. An alcoholic solution of iodine and mercuric chloride was found to give better satisfaction than iodine alone. The standard solution was prepared by dissolving 25 grams of iodine and 30 grams of mercuric chloride, each in a half litre of 95 per cent. alcohol and uniting the solutions. After standing from 6-12 hours the strength of the solution was determined by means of a standard sodium hyposulphite solution.

An oil is examined by weighing out from .2 to .8 gram and dissolving in ten cubic centimetres of chloroform; an excess of standard iodine solution is added, and after standing from 1½ to 2 hours the excess of iodine solution determined by means of the sodium hyposulphite solution. By a simple calculation the number of grams of iodine taken up by 100 grams of fat is determined, and this number is a constant for the fat examined. Hübl has determined this constant for a large number of oils and fats. The following are some of his results:

Linseed oil	.	.	.	158.
Walnut oil	.	.	.	143.
Poppyseed oil	.	.	.	136.
Cottonseed oil	.	.	.	106.
Rapeseed oil	.	.	.	100.
Olive oil	.	.	.	82.8
Lard	.	.	.	59.
Oleomargarine	.	.	.	55.3
Palm oil	.	.	.	51.5
Tallow	.	.	.	40.
Butter	.	.	.	31.
Cocoanut oil	.	.	.	8.9
Japanese wax	.	.	.	4.2

¹ Dingler's Polytechnisches Journal 253, 281.

The method affords a ready means of determining the nature of a fat. In case of a mixture of two known fats or oils the proportion of each present can be readily calculated. Thus let x be the per cent. of one fat and y that of the other, then $x + y = 100$; and if m is the iodine constant for the fat x , and n that of the fat y , and if the number found for the mixture is J ; then the quantity of the fat x present in mixture is readily calculated from the equation

$$x = \frac{100(J - n)}{m - n}$$

For example, a commercial olive oil gave on examination 97 as the iodine constant, it was therefore adulterated with a considerable quantity of some other oil. The melting point of the free fatty acids was found to be 30° . This indicated the presence of cottonseed oil, which was confirmed by other tests. Then by substituting in the above formula, the quantity of cottonseed oil present was found to be 60 per cent.

E. H. K.

Combined Carbon in Iron and Steel.

In 1875 Messrs. Schützenberger and Bourgeois studied¹ the properties of the residue obtained by treating cast-iron with copper sulphate, and found that the combustible carbon, which had up to that time been considered pure, is a compound, the composition of which can be expressed by the formula $C_{11}H_6O_3$. Lately Zabdoudsky applied himself to the same task and published his results in the *Bulletin de la Société chimique de Paris*.² He examined a specimen of pure Swedish specular iron, containing no phosphorus, sulphur nor graphite, but containing .23 per cent. of silicon and 4.10 per cent. of combined carbon. The metal was finely pulverised and treated with a mixture of sulphate of copper and chloride of sodium. The carbonaceous residue amounted to 5.76 per cent. of the weight of iron taken. This residue was analysed and found to contain 71.60 per cent. of carbon, 26.90 per cent. of water and 1.25 per cent. of siliceous material. The analysis of the carbonaceous portion gave the following result:

Carbon,	.	.	72.49 per cent.
Water,	.	.	27.27
			<hr/>
Total,			99.72

Its composition may be expressed by the formula $C_{12}H_6O_3$, a result that corresponds very closely with that obtained by Schützenberger and Bourgeois. This compound burns readily in

¹ *Comptes Rendus* **80**, 1875, p. 911.

² **41**, 9, p. 424.

the air. Heated to 150° in a sealed tube it does not change. At 200° it loses 6.5 per cent. in weight, and 18.1 per cent. at 325° .

On analysis it now yields :

Carbon,	.	.	84.51 per cent.
Hydrogen,	.	.	2.29
Oxygen,	.	.	13.20

Thus the composition is changed by the loss of water and of a considerable portion of carbon.

If heated in a stream of hydrogen there is in addition to the disengagement of hydrogen and oxygen a partial separation of carbon. Thus the residue, which after losing 24.1 per cent. of its original weight yields on analysis carbon 87.08 per cent., hydrogen 2.27 per cent., and oxygen (by difference) 10.65 per cent., loses upon further heating 33.2 per cent. of its weight, and is now found to contain 96.89 per cent. of carbon and 3.08 per cent. of hydrogen, showing a loss of all its oxygen, 1.2 per cent. of its hydrogen and 7.5 per cent. of its carbon. Upon heating still higher the same tendency to part with carbon rather than hydrogen was noticed, so that it was impracticable to obtain from it pure carbon. It is insoluble in water, alcohol, ether, hydrochloric and sulphuric acids. When treated with nitric acid and warmed it dissolves completely, forming a reddish-brown product having the composition :

Carbon,	.	.	53.71 per cent.
Hydrogen,	.	.	2.95 "
Nitrogen,	.	.	2.90 "
Oxygen,	.	.	40.44 "

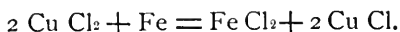
It may be represented by the formula $C_{24}H_{16}(NO_2)O_{12}$. When heated in a tube this compound decomposes, yielding hydrocyanic acid. Chlorine, bromine and iodine also form compounds with this "hydrate of combined carbon," the iodine product having the formula $C_{60}H_{29}IO_{15}$.

Decomposition of the same specimen by chloride of silver yielded a product containing 70.40 per cent. of carbon and 3.59 per cent. of hydrogen. Nor does the decomposition by the battery (according to Weyl's method) yield pure carbon. A specimen of cast-iron examined yielded a residue containing only 71.51 per cent. of carbon.

When cast-iron is treated with mercuric chloride a product is formed containing but 67.72 per cent. of carbon. Hence in determining the combined carbon in iron by Boussingault's method, an error of 32 per cent. may easily occur.

Determination of the combined carbon in steel and cast-iron.—As a result of this investigation Zaboudsky suggests that the following modification of Boussingault's method of determining carbon in steel and cast-iron be made use of:

For the purpose of decomposing the iron or steel, a dry mixture of chloride of copper and chloride of sodium is used. This mixture is obtained by evaporating to dryness a saturated solution of sulphate of copper and chloride of sodium. The metal should be finely pulverised and carefully mixed with this mixture in a mortar. Enough water should then be added to make a paste, and the mass triturated with a pestle, care being taken to keep the mortar cold. The decomposition is effected according to the equation:



Theoretically 4.8 grams of chloride of copper, or 14 grams of the mixture as prepared above, are required to dissolve 1 gram of iron. Practically, however, 20 grams of the mixture are found to be more convenient.

After half an hour's trituration the pasty mass is raised from the mortar and placed in a beaker, and the mortar washed with ferric chloride (1 pt. Fe_2Cl_6 to 4 pts. water). The glass containing the pasty mass, together with the wash water, is then heated gently, and, after warming, a little hydrochloric acid is added. This operation lasts about forty-five minutes, when the residue can be collected on a filter. This is then dried and burned in the ordinary manner. The loss in weight corresponds to the weight of the hydrated carbon and is *not* the weight of pure carbon, as was formerly supposed.

In order to obtain the true weight of the combined carbon factors must be used. These factors represent the amount of carbon in the hydrate of carbon that has been burned.

In order to determine the mean value of these factors for the various grades of iron Zaboudsky examined a large number of specimens, and gives the following numbers as representing the amount of carbon in the combustible portion of the residue obtained by treating iron and steel in the manner given above:

Pure specular cast-iron (not manganiferous),720
Ferro-manganese,700
Specular manganiferous cast-iron,685
White cast-iron,	}710
Pure grey cast-iron,		
Steel (cast for cannons and guns, containing about 5 per cent. of carbon),660
Hard steel,675
Iron,690

W. S. B.

AMERICAN CHEMICAL JOURNAL.

DETERMINATIONS OF LACTOSE IN MILKS BY OPTICAL METHODS.

BY HARVEY W. WILEY.

The usual method of determining milk sugar by evaporating the sample to dryness, and extracting the sugar with alcohol after exhausting with ether, requires a great deal of time and labor. If some reliable optical method could be devised, the determination of the lactose in milk would be the work of only a few minutes. The difficulties which are encountered in seeking for such a method are numerous and serious, so much so that little credit has heretofore been given to any of the processes of optical analysis in use. In the following paper I will give the results which have been obtained under my direction in the study of this problem. The optical work collected in the following tables was done chiefly by my assistants, Messrs. G. L. Spencer and C. A. Crampton; the alcohol extractions were made by Mr. A. E. Knorr, and the nitrogen estimation by Messrs. Fuller and Trescott.

Specific Rotatory Power of Milk Sugar.

Crystallised milk sugar when first dissolved possesses a higher rotatory power than it has in the milk from which it was derived. This increased optical activity may be compared with the original by the ratio 8 : 5, nearly. After the solution has stood for twelve to twenty hours, or immediately on boiling it, this extra rotatory

power is lost. In estimating the specific rotatory power of milk sugar the numbers given always refer to the constant and not the transient gyrotory property.

Among the earliest numbers assigned to the rotation of lactose are those of Poggiale $(a)_D = 54.2$ and Erdmann $(a)_D = 51.5$, (Sucrose $(a)_D = 66.5$). Biot¹ places this number for lactose at 60.23, and Berthelot² at 59.3 for the transition tint (a) . Hoppe-Seyler, in his "Handbuch der physiologisch-chemischen Analyse," gives this number at $(a)_j = 58.2$. Since the ratio of $(a)_D$ to $(a)_j$ is 1 : 1.1306, the above numbers become for Biot $(a)_D = 53.27$, for Berthelot $(a)_D = 52.47$, and Hoppe-Seyler $(a)_D = 51.48$. Hesse³ observed the rotation number to be $(a)_D = 52.67$, when the solution contained 12 g. per 100 cc. and the temperature was 15°. On the other hand, when the concentration is only 2 g. per 100 cc. the number assigned is $(a)_D = 53.63$. It appears from this that the specific rotation power of a solution of milk sugar diminishes with the increase of its concentration, and this view is adopted by Landolt, Tollens and Schmidt.

The following general formula⁴ is used to correct the reading of the polariscope for concentration of solution :

$$(a)_D = 54.54 - .5575 c + .05475 c^2 - .001774 c^3,$$

in which c = number grams sugar in 100 cc. solution. These observations are contradicted by the work of Schmoeger,⁵ who, in an elaborate series of experiments, using instruments of different construction and observing all necessary precautions, found the rotation number of lactose sensibly constant for all degrees of concentration up to the saturation point. In 32 series of investigations, in which the degree of concentration gradually increases from $c = 2.3554$ to $c = 36.0776$, and in which a constant temperature of 20° was maintained, the variations in the numbers obtained were always within the limits of error of observation. The mean of all these numbers fixes the value of $(a)_D$ at 52.53.

According to Schmoeger, variations in temperature have far more to do with changes in rotatory power than differences of concentration. The value of $(a)_D$ falls as the temperature rises.

¹ Compt. rend. **42**, 349.

² Dict. de Chem. par Ad. Würtz 2, 2d part, p. 188.

³ Annal. Chem. u. Pharm. **176**, 98.

⁴ Tucker, Sugar Analysis, 91.

⁵ Berichte der deutsch. chem. Gesell. 1830, 1922 et seq.

Under 20° the disturbing influence of temperature is greater than above 20° . At the latter degree $(a)_D$ varies inversely about .075 for each 1° change of temperature. Pellet and Biard,¹ as a result of their observations, fix the rotatory power of milk sugar at 58.94 for $(a)_D$ ($(a)_D = 52.12$).

After a careful review of the methods used in the above *résumé* and the numbers determined by them, I am inclined to accept the mean obtained by Schmoeger as the one entitled to the greatest credit. It also has the advantage of being almost the mean of all the various numbers which have been assigned as the specific rotating power of lactose, viz.

Poggiale,	.	.	54.2
Erdmann,	.	.	51.5
Biot,	.	.	53.27
Berthelot,	.	.	52.47
Hoppe-Seyler,	.	.	51.48
Hesse,	.	.	52.67
"	.	.	53.63
Schmoeger,	.	.	52.53
Pellet and Biard,	.	.	52.12

Mean, 52.65

In the present state of our knowledge, therefore, the specific rotatory power of milk sugar should be taken at $(a)_D = 52.5$. I propose, at an early date, to make a careful study of this subject, in order to fix, if possible, an exact number for the expression of the rotating power, and to examine the conflicting evidence respecting the influence of the degree of concentration on the same. The estimation of lactose in milk by the polariscope is rendered difficult also by the presence in milk of various albumens—all of which turn the plane of polarisation to the left. As will be seen by the data given further along, the ordinary method of removing these albumens, viz. by a solution of basic lead acetate, is far from being perfect. If, therefore, a portion of the albumen be left in the liquid submitted to polarisation, the rotation to the right will be diminished by its presence.

Hoppe-Seyler² assigns as the rotation power of egg albumen $(a)_D = -35.5$, and for serum albumen $(a)_D = -56$. Both acids

¹ Bull. de l'Assoc. des Chimistes 1, 5, 171 et seq. ² Würtz, Dictionnaire de Chimie 1, 91.

and alkalies seem to increase the rotating power, which may with acetic acid reach $(a)_D = -71$.

Fredericq¹ gives the rotation number for blood serum for the rabbit, cow and horse at $(a)_D = -57.3$, and for the dog at -44 . Paraglobulin, according to the same author, has a rotation number $(a)_D = -47.8$.

Milk albumen² has the following numbers assigned to it:

Dissolved in MgSO_4 sol.	$(a)_D = -80$
“ “ dil. HCl.	“ $= -87$
“ “ dil. NaOH sol.	“ $= -76$
“ “ strong KOH sol.	“ $= -91$

The hydrates of albumen³ have rotation powers which vary from $(a)_D = -71.40$ to $(a)_D = -79.05$. From the chaotic state of knowledge concerning the specific rotating power of the various albumens, it is impossible to assign any number which will bear the test of criticism. For the purposes of this paper, however, this number may be fixed at $(a)_D = -70$ for the albumens which remain in solution in the liquids polarised for milk sugar.

The phenomenon of “birotation” in milk sugar has already been noticed. The problem of analysis of this sugar is, however, still further complicated by the facts pointed out by Schmoeger⁴ and Erdmann⁵ that when milk is rapidly evaporated in a plain dish the sugar is left in the anhydrous state, and that this sugar in fresh solutions exhibits the phenomenon of “half rotation.” When such sugar is extracted with alcohol and re-evaporated, it, doubtless, is still anhydrous. But in the calculation of results this sugar is generally estimated as containing water of crystallisation, and thus an error, which Schmoeger reckons at as much as .2 per cent., is introduced into the results. This fact, not well recognised, combined with the knowledge that in the process of evaporation many particles of sugar must be occluded by the hardening caseine, tends to throw doubt upon the accuracy of estimating the sugar by the extraction method.

The work which I undertook had for its object the determination of the best method of preparing the milk-sugar solution for

¹ Compt. rendus, 93-465.

² Hoppe-Seyler in Handbook of the Polariscopes, Landolt, p. 248.

³ Kühne and Chittenden, Am. Chem. Journal 6, 45.

⁴ Ber. d. deutsch. chem. Gesell., 1880, 1915 et seq.; 1881, 212 et seq.

⁵ Ber. d. deutsch. chem. Gesell., 1880, 2180 et seq.

the polariscope, and a comparison of the numbers obtained by this instrument with those given by the ordinary process of extraction.

The reagents used for removing the albumens were :

- (1) Saturated solution basic lead acetate, sp. gr. 1.97.
- (2) Nitric acid solution of mercuric nitrate diluted with an equal volume of water.
- (3) Acetic acid, sp. gr. 1.040, containing 29 per cent. $\text{HC}_2\text{H}_3\text{O}_2$.
- (4) Nitric acid, sp. gr. 1.197, containing 30 per cent. HNO_3 .
- (5) Sulphuric acid, sp. gr. 1.255, containing 31 per cent. H_2SO_4 .
- (6) Saturated solution sodium chloride.
- (7) Saturated solution magnesium sulphate.
- (8) Solution of mercuric iodide in acetic acid ; formula¹ KI , 33.2 g. HgCl_2 , 13.5 g.

Strong $\text{HC}_2\text{H}_3\text{O}_2$,	20.0 cc.
Water,	640 cc.

Alcohol, ether and many solutions of mineral salts, hydrochloric and other acids were also tried as precipitants for albumen, but none of them presented any advantages which would make a detailed account of the experiments of any interest.

TABLE NO. I.

This table contains a record of the experiments which led to the adoption of 1 cc. acetate of lead solution, or 1 cc. acid mercuric nitrate, as the best amount of each for 50 cc. of milk.

Nearly all the polarisations were made in a 400 mm. tube. From two to four observations were made with each sample. An average of these readings was taken for each determination. In the calculations the value of $(a)_d$ was taken at 53 instead of 52.5, the number which subsequent investigations have led me to believe more exact. The instrument employed was a "Laurent Large Model" polariscope.

In all cases the volume of the solution was corrected for the volume of the precipitated caseine. This volume was assumed to occupy 2 cc. for each 50 cc. milk.

Since in the Laurent instrument the weight of sucrose in 100 cc. to read even degrees on the scale is 16.19 g. [$(a)_d = 66.67$], it follows that the weight of lactose in 100 cc. to read one degree on the

¹Journal de Pharmacie et de Chimie, Aug. 1884, 108.

TABLE I.
Reagents Employed in Precipitating Albumens.

Reagents Employed in Precipitating Albumens.										
Per cent. lac- tose extracted by alcohol.	Pb 1 cc.	Pb 2 cc.	Pb 3 cc.	Pb 4 cc.	Pb 5 cc.	A 5 cc.	Other Reagents.			
	Per cent. Lactose.									
4.57				{ 10 cc.	3.67	4.23				
4.52				{ 2.45	3.57	4.14				
4.46	4.48					3.57				
3.92	4.19				3.35					
4.35		3.55				4.32				
3.71	4.01					3.00				
4.10	{ 4.63					{ 4.44				
	4.96 H					{ 4.68 H				
4.16	{ 4.29					{ 3.80				
	4.33					{ 3.67 H				
4.48	{ 4.59					{ 4.04				
	4.58 H					{ 4.12 H				
4.10	4.12 H					3.47 H				
4.80	4.87 H			(4 cc.)		4.44 H				
4.77	5.02 H	4.82 H	4.50 H	4.31 H			4 cc.	5 cc.	6 cc.	8 cc.
							4.70 H	4.76 H	4.76 H	4.78
4.25	4.25	3.75	3.38	3.38			3.97	3 cc.		
								3.89		
4.22	4.90 H	4.58 H						HNO ₃		
3.14	{ 4.40						4.68 H	4.66 H	4.50 H	
	4.32 H									
3.30	4.43 H									
4.72	4.45	4.18	3.87	3.65	3.26		3.96	{ 3.98		3.88
								3.98		
								3.88 H		
4.88	{ 4.87					4.37		4.27		
	4.87 H					4.25	(5 cc.)	4.43	H ₂ O ₄	
4.31	4.71					{ 4.43	4.51	4.59		
	4.86 H					{ 4.43 H	4.79 H	4.59 H		
4.39	4.11									
4.70	4.17									
4.96	{ 4.93					{ 4.45		{ 4.69		
	4.97 H					4.43 H		4.67 H		
4.60	{ 4.41					{ 3.86	{ 3.90	{ 3.94		
	4.45					3.86	3.90	4.10		
4.74	{ 4.41					{ 4.21	{ 4.32	{ 4.32		
	4.45 H					4.35 H	4.44 H	4.55 H		
4.59	{ 4.33					{ 3.94	{ 4.03	{ 3.98		
	4.37 H	{ NaCl	1 cc. MR			3.93 H	4.10 H	4.10 H		
4.39		4.29 H	4.29 H							
4.60	4.18 H		4.66							
4.26	3.67 H		4.09							

scale for each per cent. lactose present would be 16.19, $x = 53$; 66.67, $x = 20.37$.

If 52.5 be taken as the value of $(a)_D$ for lactose, then $x = 20.56$.

In table No. I, A indicates acetic acid, Pb basic acetate of lead, MR acid mercuric nitrate, etc. The letters C and H indicate the temperature; C denoting the ordinary temperature of the room, and H that the sample was heated to 100° and cooled before filtering.

The numbers obtained by extraction with alcohol are taken as the basis of comparison, not because I believe them to be more reliable, but because that method is the one generally employed in the estimation of milk sugar.

In the alcohol extraction the milk was evaporated to dryness in a thin glass capsule, the dish and dried residue pulverised in a mortar, washed with ether into a continuous extraction apparatus, exhausted with ether, and then with 80 per cent. alcohol for ten hours.

Duplicate analyses are indicated in the table by the small brackets.

Remarks on Table I.

The results obtained by using various other reagents for the precipitation of the caseine, viz. $MgSO_4$, $CuSO_4$, HCl , etc., have not been entered in the table. In none of these cases was there sufficient encouragement to warrant an extended trial. In most cases the precipitation was slow or imperfect, and the filtration difficult.

One important fact should not be overlooked, viz. that any excess of basic plumbic acetate causes a rapid decrease in the rotatory power of the solution; whether this decrease is due to precipitation of the sugar or solution of the albumens does not clearly appear. Illustrations of this decrease are seen in analyses 2, 12, 13 and 17.

It seems to make little difference whether the precipitation is made hot or cold. The question of temperature is set forth in greater detail in the next table. From all the experiments made it clearly appeared that the best optical results are obtained by the use of a minimum quantity of basic lead acetate, or of either the acid mercuric nitrate or iodide. For 50 to 60 cc. of milk, 1 cc. of the lead acetate or mercuric nitrate solution of the strength noted,

and 25 cc. of the mercuric iodide solution are the proper quantities. It makes no difference, however, if a large excess of the two latter reagents is employed. Of the three the last is to be preferred.

TABLE NO. II.

In this table will be found the results of the comparative determinations of milk sugar by extraction with alcohol, by precipitation with 1 cc. basic lead acetate, and the same with 1 cc. acid mercuric nitrate, hot and cold, to each 60 cc. of milk.

In many of the analyses the large differences in results by the three methods show a fault of manipulation, but all the results have been given without selection.

TABLE II.

No.	Reagents Employed.				
	Extract by Alcohol.	C. Pb 1 cc.	H. Pb 1 cc.	C. MR 1 cc.	H. MR 1 cc.
Percentage of Milk Sugar.					
1	4.55		4.74		4.92
2	4.10		4.22		4.50
3	4.51	4.54	4.22	4.68	4.62
4	4.36	4.55	4.53	4.89	4.90
5	4.05	4.14	4.09	4.48	4.39
6	3.84		3.84	3.98	3.98
7	4.52	4.67	4.73	5.01	5.00
8	4.25	4.21	4.26		4.51
9	4.45	4.61	4.54	4.87	4.87
10	4.92	5.20	5.22	5.43	5.47
11	3.84		3.72	4.00	3.96
12	4.53	4.61	4.64	4.87	4.85
13	4.57	4.54	4.55	4.91	4.84
14	4.66	4.29	4.45		4.63
15	4.17	3.65	3.75	3.95	3.87
16	5.02	4.66	4.64	4.86	4.86
17	4.68	4.03	3.94	4.39	4.37
18	4.23	3.82	3.89	4.08	4.02
19	4.96	4.70	4.84	5.04	5.04
20	4.85	4.39	4.41	4.53	4.65
21	4.63	4.47	4.47	4.69	4.67
22	4.47	4.39	4.45	4.67	4.71
23	4.46	4.23	4.31	4.65	4.63
24	4.47	4.59	4.67	5.01	4.95

No.	Extract by Alcohol.	C. Pb 1 cc.	H. Pb 1 cc.	C. MR 1 cc.	H. MR 1 cc.
25	4.40	4.41	4.55	4.45	
26	4.85	4.67	4.73	4.97	
27	4.45	4.21	4.33	4.57	
28	4.44	3.98	4.10	4.28	
29	4.10	4.21		4.55	
30	4.38	5.57	4.69	4.89	
31	4.20	4.21	4.37	4.57	
32	4.69	4.59	4.67	4.89	
33	4.52	4.27	4.41	4.41	
34	4.37	4.65	4.93	4.93	
35	4.52	4.27	4.41	4.56	
36	4.88	4.83	4.93	5.17	
37	4.61	4.30	4.43	4.57	
38	4.79	4.59	4.67	4.91	
39	4.67	4.26	4.41	4.51	
40	4.79	4.64	4.74	4.94	
41	3.95	4.10	4.26	4.38	
42	4.00	4.61	4.61	4.77	
43	4.63	4.24	4.37	4.57	
44	4.77	4.64	4.70	4.94	
45	4.85		4.53	4.73	
46	4.71		4.67	4.93	
47	4.34	4.06	4.12	4.40	
48	4.05	4.67	4.77	4.83	
49	3.67	4.12	4.18	4.36	
50	3.78	4.58	4.62	4.82	
51	4.19	4.27	4.57	4.53	
52	3.83	4.68	4.78	4.97	
53	3.86	3.97	4.07	4.21	
54	4.59	4.59	4.61	4.83	
55	4.02	4.26	4.36	4.40	
56	4.36	4.62	4.76	4.94	
57	4.20	4.18	4.28	4.48	
58	4.09	4.52	4.56	4.74	
59	4.09		4.28	4.46	
60	4.12		4.49	4.81	
61	4.20		4.33	4.41	
62	4.45		4.25	4.77	
63	4.33		4.09	4.37	
64	4.62		4.33	4.99	
Mean,	4.33	4.34	4.38	4.58	4.63

In the following table will be found the percentage of milk sugar obtained by using varying quantities of the mercuric iodide reagent,

and a comparison of the results obtained with those given by the use of acid mercuric nitrate and basic plumbic acetate.

TABLE III.

Reagents Employed.

No.	PbA	MR	Mercuric Iodide.			
			20 cc.	26 cc.	30 cc.	35 cc.
Percentage of Milk Sugar.						
1	4.28	4.48	4.56	4.56		
2	4.46	4.57	4.62	4.66		
3	4.37	4.65	4.63	4.63	4.60	4.65
4	4.37	4.53	4.60	4.53	4.63	4.60
5	4.38	4.63	4.50	4.53	4.53	4.59
6	4.33	4.67	4.43	4.53	4.60	4.66
7	4.30	4.67	4.67	4.67	4.59	4.57
8	4.33	4.59	4.50	4.53	4.50	4.59
9	4.27	4.60	4.63	4.60	4.66	4.66
	4.34	4.60	4.57	4.58	4.61	4.62

Albumen remaining in Filtrate from Lead Acetate and Mercuric Iodide Solutions.

From the fact that the polariscopic readings show that solutions of milk prepared with lead acetate have a lower rotating power than those prepared with mercury salts, it is to be inferred that the lead reagent either leaves certain soluble and transparent kinds of albumen in solution, or else dissolves a portion of those which are at first precipitated. To test the accuracy of this supposition a few analyses were made to determine the amount of albumen left in the filtrate from the lead and mercury reagents. At the same time different quantities of the mercuric iodide solution were used, in order to determine the amount which would give the best results. For 60 cc. milk the quantity of mercuric iodide to be used should be 25 to 30 cc.

In the following table will be found the percentages of albumen in the whey after precipitating with the reagents noted and filtering. Ten cc. of the filtrate were evaporated to dryness in a thin glass dish, and the dried residue (with the glass) burned with soda lime. The calculated nitrogen was then multiplied by 6.25 and the product taken as the percentage of albumen.

TABLE IV.

Per cent. albumen in filtrate from PbA.	Per cent. albumen in filtrate from HgI ₂ . 15 cc.	Per cent. albumen in filtrate from HgI ₂ . 20 cc.	Per cent. albumen in filtrate from HgI ₂ . 25 cc.	Per cent. albumen in filtrate from HgI ₂ . 30 cc.	Per cent. albumen in filtrate from HgI ₂ . 35 cc.
.0865	.195	.0865	.0865	.0562	.0865
.113	.0674	.0865	.0865	.0865	.0865
.113	.0674	.0562	.113	.0562	.0312
.0865	.0674	.0562	.113	.0562	.0562
.113	.0674	.0562	.0312	.0865	.0562
.113	.009	.0865	.03	.0862	.1412
.113		.1412	.113	.1412	.0562
.195		.1412	.113	.1412	.1412
.113		.1412	.0865	.1412	.0865
.1412		.113	.1412	.113	.0865
.113		.1362	.009		
		.125			
		.009			
		.009			
Mean, .1182	.0789	.0888	.0839	.0964	.0828

In table No. V will be found percentages of albumen remaining in filtrate from lead acetate precipitation of forty-two samples taken from those represented in table No. II. From these two tables it is at once seen that the quantity of laevo-rotatory matter remaining in milk after treatment with basic lead acetate is much greater than in those samples treated with the two mercuric salts. This explains at once the higher per cent. of milk sugar obtained by using the last-named reagents, and shows that the use of lead acetate as a clarifying agent must be abandoned.

Per cent. Albumen after Precipitation by Lead Acetate.

No.	Pr ct.	No.	Pr ct.	No.	Pr ct.
1	.250	15	.271	29	.350
2	.306	16	.237	30	.374
3	.135	17	.237	31	.329
4	.272	18	.169	32	.305
5	1.34	19	.103	33	.305
6	.239	20	.271	34	.237
7	.301	21	.237	35	.305
8	.305	22	.271	36	.339
9	.237	23	.235	37	.237
10	.339	24	.271	38	.374
11	.271	25	.237	39	.203
12	.305	26	.237	40	.373
13	.267	27	.271	41	.305
14	.237	28	.339	42	.339

Mean, .278

Comparison of Results obtained by Extraction with Alcohol and Polarisation.

By consulting table II it will be seen that the percentage of sugar obtained by extraction with alcohol is practically the same as that got by polarisation of the lead acetate filtrate.

Thus, the mean percentage of sugar by alcohol (65 analyses) is 4.32; by lead acetate, cold (53 analyses) is 4.34; by lead acetate, hot (64 analyses) is 4.38; by mercuric nitrate, cold (61 analyses) is 4.58; by mercuric nitrate, hot (24 analyses) is 4.63.

If now the milk sugar, as has already been intimated, exists in an anhydrous state after extraction with alcohol, the percentage of it after the addition of the molecule of water would be increased. Thus molecular weight of anhydrous milk sugar 342: mol. wt. of the hydrous from $360 = 4.38 : x$, whence the value of $x = 4.61$. This agrees very nearly with the number obtained by acid mercuric nitrate.

By a study of table V it is found that mercuric iodide gives nearly the same rotatory power as mercuric nitrate, and also that by combustion the filtrates from the milks clarified by lead acetate contain more albumen than those prepared with mercuric iodide. There is, therefore, every reason for believing that the numbers given by the mercury salts are nearer the truth than those from the lead.

It may be urged that the increased rotatory power observed by the mercury salts is due to the conversion, by the dilute acids, of a part of the lactose into galactose, which has a rotatory power greater than that of milk sugar. But when it is remembered that the quantity of acid introduced is extremely minute, that the samples need not be warmed, that they can be filtered and polarised within a few minutes of the time of the introduction of the reagents, the suggestion is seen to be of no force.

For example, in the acid mercuric nitrate it was found that the percentage of sugar was the same whether one, five or ten cc. of the reagent were employed, and whether it was polarised immediately or after heating and cooling. It is evident that one cc. of the reagent, containing less than a half cc. of nitric acid and diluted in 100 cc. of liquid, could not exert any notable effect on the rotatory power of the solution.

In the mercuric iodide solution 20 cc. of acetic acid are used for every 660 cc. of the reagent.

Thirty cc. of this reagent contain, therefore, about one cc. of acid. This in 100 cc. of liquid, immediately filtered and polarised, could not affect in any marked degree the rotatory power.

Since combustion with soda lime shows that the filtrate from the mercuric iodide sample is practically free from albumen, it is evident that the numbers obtained in this way must be a near approximation to the truth.

The Process of Analysis.

The reagents, apparatus and manipulation necessary to give the most reliable results in milk sugar estimation are as follows :

Reagents.—1. *Basic plumbic acetate*, sp. gr. 1.97. Boil a saturated solution of sugar of lead with an excess of litharge, and make it of the strength indicated above. One cubic centimetre of this will precipitate the albumens in 50 to 60 cc. of milk.

2. *Acid mercuric nitrate* dissolves mercury in double its weight of nitric acid, sp. gr. 1.42. Add to the solution an equal volume of water. One cubic centimetre of this reagent is sufficient for the quantity of milk mentioned above. Larger quantities can be used without affecting the results of polarisation.

3. *Mercuric iodide with acetic acid* (composition already given).

Apparatus.

1. Pipettes marked at 59.5, 60 and 60.5 cc.
2. Sugar flasks marked at 102.4 cc.
3. Filters, observation tubes and polariscope.
4. Sp. gr. spindle and cylinder.
5. Thermometers.

Manipulation.

1. The room and milk should be kept at a constant temperature. It is not important that the temperature should be any given degree. The work can be carried on equally well at 15°, 20° or 25°. The slight variations in rotatory power within the above limits will not affect the result for analytical purposes. The temperature selected should be the one which is most easily kept constant.

2. The sp. gr. of milk is determined. For general work this is done by a delicate sp. gr. spindle. Where greater accuracy is required use sp. gr. flask.

3. If the sp. gr. be 1.026 or nearly so, measure out 60.5 cc. into the sugar flask. Add 1 cc. of mercuric nitrate solution or 30 cc. mercuric iodide solution and fill to 102.4 cc. mark. The precipitated albumen occupies a volume of about 2.4 cc. Hence the solution is really 100 cc. If the sp. gr. is 1.030 use 60 cc. of milk. If sp. gr. is 1.034 use 59.5 cc. milk.

4. Fill up to mark in 102.4 cc. flask, shake well, filter and polarise.

Notes.

In the above method of analysis the specific rotatory power of milk sugar is taken at 52.5, and the weight of it in 100 cc. solution to read 100 degrees in the cane sugar scale at 20.56 grams. This is for instruments requiring 16.19 grams sucrose to produce a rotation of 100 sugar degrees. It will be easy to calculate the number for milk sugar whatever instrument is employed.

Since the quantity of milk taken is three times 20.56 grams, the polariscopic readings divided by 3 give at once the percentage of milk sugar when a 200 mm. tube is used.

If a 400 mm. tube is employed, divide reading by 6; if a 500 mm. tube is used, divide by 7.5.

Since it requires but little more time, it is advisable to make the analysis in duplicate, and take four readings for each tube. By following this method gross errors of observation are detected and avoided.

By using a flask graduated at 102.4 for 60 cc. no correction for volume of precipitated caseine need be made. In no case is it necessary to heat the sample before polarising.

THE CHEMICAL COMPOSITION OF WHEAT AND CORN AS INFLUENCED BY ENVIRONMENT.

BY CLIFFORD RICHARDSON.

During the past two years an examination of a large number of American wheats and corns has been completed in the laboratory of the United States Department of Agriculture.

The specimens, collected from all parts of the country and grown under the most varied conditions, have afforded an opportunity for the study of the effects of soil, climate and methods of cultivation upon the chemical composition and physical condition of the two cereals.

It is my intention here to give a *résumé* of the principal results of the work, referring for details to the original reports, which can be had by application to the Department of Agriculture at Washington.

Wheat.

Four hundred and seven analyses of wheat are included in our tables, and from them the averages have been drawn for the composition and weight per hundred grains of the wheats of the whole country, of different sections and for particular States, which are given in the tables below.

In two hundred and sixty of the samples the oil and fibre were determined, and from these analyses, made in 1882, averages, including these constituents and the carbohydrates, have been calculated.

From the preceding analyses the following facts are derived. American wheats are deficient in albuminoids as compared with those of foreign countries. They are, too, lighter in weight per hundred grains; they contain less water, about the same percentage of ash, more oil, and a smaller amount of fibre. For comparison the averages for foreign grain are given.

The smaller amount of water in our wheats is due, undoubtedly, to a drier climate. The question of hygroscopicity will, however, be considered in another paper.

The average amount of ash differs very little in wheats from our own and from foreign countries, but among the individual analyses many specimens of grain grown on new and rich soil will be found which have an increased amount of this constituent.

In oil our wheats are much richer, but the question arises whether the more complete methods of extraction of the present day make the results entirely comparable.

The amount of fibre is decidedly smaller, as was found to be the case in American grasses. This, in both cases, is due to our hotter summers and shorter period of growth.

AVERAGE COMPOSITION OF AMERICAN WHEATS.

Locality.	Number of analyses.	Number of weights.	Weight of 100 grains.	Water.	Ash.	Undetermined.*	Albuminoids.	Nitrogen	Weight of 100 grains.		Albuminoids.	
									Highest.	Lowest.	Highest.	Lowest.
			Grams.	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Grams.	Grams.	Per Cent	Per Cent
U. S. and British America.....	407	377	3.644	10.16	1.92	75.77	12.15	1.94	5.924	1.830	18.03	7.70
Atlantic and Gulf States.....	117	105	3.489	10.34	1.77	76.54	11.35	1.81	5.079	1.830	15.58	9.43
Middle States.....	91	89	3.537	10.01	1.85	75.04	12.50	2.00	5.800	2.138	16.63	10.15
Western States.....	177	166	3.763	9.83	2.06	75.37	12.74	2.04	5.924	2.561	18.03	8.93
Pacific States.....	20	15	4.901	10.25	1.87	78.15	9.73	1.56	5.745	2.584	12.78	7.70
Canada.....	6	...	3.325	9.74	1.56	77.83	10.87	1.74	3.686	2.964	14.70	9.45
Pennsylvania.....	33	26	3.373	10.73	1.70	76.13	11.44	1.83	4.658	2.035	15.58	9.45
Maryland.....	9	...	3.597	10.52	1.75	76.08	11.65	1.86	5.079	3.075	14.53	9.80
Virginia.....	15	14	3.433	9.98	1.84	76.08	12.10	1.93	4.283	1.830	14.00	10.15
West Virginia.....	2	1	3.392	8.55	2.07	78.44	10.94	1.75	11.03	10.85
North Carolina.....	22	...	3.776	10.03	1.59	77.95	10.43	1.67	4.628	2.780	12.43	8.93
Georgia.....	7	...	3.579	10.00	1.96	76.26	11.78	1.89	4.627	2.834	14.00	9.45
Alabama.....	19	19	3.424	10.82	1.96	75.93	11.29	1.80	4.647	2.011	13.65	9.80
Ohio.....	44	44	3.476	10.68	1.94	74.55	12.83	2.05	5.800	2.663	16.10	10.68
Tennessee.....	15	14	3.150	10.24	1.92	75.34	12.50	2.00	3.990	2.138	16.63	10.15
Kentucky.....	8	...	3.454	10.83	1.75	74.27	13.15	2.10	3.666	3.146	14.53	11.90
Michigan.....	22	...	3.969	10.71	1.64	75.98	11.67	1.87	4.902	3.402	15.23	10.50
Missouri.....	12	...	3.502	9.80	1.92	76.72	11.56	1.86	3.867	3.098	14.00	10.50
Arkansas.....	1	9.56	2.52	74.97	12.95	2.07
Minnesota.....	13	13	3.245	9.96	1.77	75.08	13.19	2.11	3.867	2.720	17.15	10.85
Dakota.....	12	12	3.149	8.84	1.96	74.25	14.95	2.40	3.700	2.771	18.03	12.43
Manitoba.....	2	2	3.288	8.35	1.63	75.49	14.53	2.32
Kansas.....	10	...	3.304	11.80	1.64	75.41	11.15	1.78	3.424	2.881	12.25	10.50
Texas.....	19	...	2.847	10.03	1.81	75.02	13.14	2.03	3.937	2.561	15.23	10.68
Colorado.....	106	98	4.214	9.73	2.21	75.33	12.73	2.10	5.924	2.716	15.94	8.93
Utah.....	2	2	3.893	9.17	2.23	78.45	10.15	1.62	4.084	3.703	10.50	9.80
New Mexico.....	2	2	3.572	9.30	1.98	78.22	10.50	1.68	3.956	3.188	11.73	9.28
California.....	10	10	3.892	10.73	1.86	76.47	10.94	1.75	5.184	3.095	12.78	9.10
Oregon.....	8	...	5.044	9.74	1.84	79.82	8.60	1.37	5.745	4.253	9.47	8.05
Washington Territory.....	2	2	3.655	9.89	1.98	79.90	8.23	1.32	4.726	2.584	8.75	7.70

* Fibre, carbohydrates and fat.

AVERAGE COMPOSITION OF AMERICAN WHEATS.

No. of analyses.	Locality.	Weight of 100 grains.	Water.		Ash.		Oil.		Carbohydrates.		Fibre.		Albuminoids.		Nitrogen.		Heaviest 100 grains.		Lightest 100 grains.		Highest albuminoids.		Lowest albuminoids.	
			Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
260	United States and Canada...	3.638	10.27	1.84	2.16	71.98	1.80	11.95	1.91	5.924	1.830	17.15	8.05											
108	Atlantic and Gulf States...	3.464	10.42	1.75	2.17	72.61	1.72	11.33	1.81	5.079	1.830	15.58	9.45											
47	The Middle West.....	3.607	10.51	1.76	2.01	71.67	1.90	12.15	1.94	4.902	2.138	16.63	10.15											
97	West of the Mississippi....	3.806	10.04	1.99	2.22	71.12	1.87	12.76	2.04	5.924	2.561	17.15	10.15											
8	The Pacific coast.....	5.044	9.74	1.84	2.08	76.18	1.56	8.60	1.37	(5.745)	(4.253)	9.47	8.05											
6	Canada	3.325	9.74	1.56	2.29	73.87	1.97	10.87	1.74	3.686	2.964	14.70	9.45											
32	Pennsylvania	3.373	10.72	1.67	2.05	72.45	1.73	11.38	1.82	4.658	2.035	15.58	9.45											
9	Maryland	3.597	10.52	1.75	2.09	72.25	1.74	11.05	1.86	5.079	3.075	14.53	9.80											
11	Virginia	3.343	10.34	1.70	2.21	71.87	1.71	12.71	1.95	4.208	1.830	14.00	10.15											
7	Georgia.....	3.579	10.00	1.96	2.30	72.24	1.72	11.78	1.89	4.627	2.834	14.00	9.45											
22	North Carolina	3.776	10.03	1.59	2.25	73.94	1.76	10.43	1.67	4.628	2.780	12.43	8.93											
17	Alabama.....	3.314	10.94	2.03	2.21	71.84	1.62	11.30	1.79	4.647	2.011	13.65	9.80											
Michigan (Kedzie).....		11.28	1.73	74.97	12.02	1.92	13.78	9.13											
22	Michigan.....	3.969	10.71	1.64	2.06	72.12	1.80	11.67	1.87	4.902	3.402	15.23	10.50											
8	Kentucky	3.454	10.83	1.75	1.87	70.37	2.03	13.15	2.10	3.666	3.146	14.53	11.90											
14	Tennessee ..	3.150	10.19	1.89	2.00	71.33	2.02	12.51	2.00	3.990	2.138	16.63	10.15											
12	Missouri.....	3.502	9.80	1.92	2.19	72.36	2.17	11.56	1.86	3.867	3.098	14.00	10.50											
9	Minnesota.....	3.354	10.60	1.71	2.03	70.96	2.04	12.66	2.03	3.828	3.116	17.15	10.85											
10	Kansas	3.204	11.80	1.64	1.98	71.35	2.08	11.15	1.78	3.424	2.881	12.25	10.50											
19	Texas	2.847	10.03	1.81	2.11	70.85	2.06	13.14	2.10	3.937	2.561	15.23	10.68											
45	Colorado.....	4.682	9.57	2.21	2.38	70.91	1.62	13.31	2.13	5.924	3.851	15.94	11.19											
8	Oregon.....	5.044	9.74	1.84	2.08	76.18	1.56	8.60	1.37	5.745	4.253	9.47	8.05											

AVERAGE COMPOSITION OF FOREIGN WHEATS.

Locality.	Authority.	No. of analyses.	Water.	Ash.	Oil.	Carbhy- drates.	Fibre.	Albumi- noids.	Highest al- buminoids.	Lowest al- buminoids.
Russian.....	Laskowsky	24	Per cent. 11.49	Per cent.	Per cent. 1.57	Per cent.	Per cent.	Per cent. 19.48	Per cent. 24.56	Per cent. 10.68
German.....	Wolff.....	14.40	1.70	1.50	66.40	3.00	13.00
Continental	Peliget.....	14	14.00	1.60	1.20	66.90	1.70	14.60	21.50	10.60
do.	Millon.....	16	13.82	1.57	1.74	70.13	1.70	11.04	13.81	9.92
do.	Reiset.....	20	14.43	1.99	70.58	13.00	17.94	10.69
World	König	200	13.56	1.79	1.70	67.87	2.66	12.42	24.16	8.19
do.	Kühn.....	14.30	1.70	1.60	66.20	3.00	13.20	24.10	8.20

Maxima and minima of albuminoids, percentage of nitrogen, and weight of 100 grains of wheat.

No. of analyses.	Locality.	Authority.	Per cent. of nitro- gen.	Per cent. of al- buminoids.	Albuminoids.	Weight of 100 grains.		
					Maximum.	Minimum.	Average.	Minimum.
					Per cent.	Per cent.	Grams.	Grams.
25	North German.....	Von Bibra.....	2.20	13.76	18.25	9.80	4.270	7.450
20	South German.	do.	2.13	13.28	17.81	9.68	4.473	7.000
14	Scotch.....	do.	2.07	12.95	14.63	11.06	4.679	5.200
5	Egypt.....	do.	1.46	9.10	9.04	8.75	3.855
2	Australian.....	do.	1.60	9.98	9.94	9.94
13	Algerian.....	do.	2.20	13.75	15.50	11.25	5.540	6.525
9	Spanish	do.	2.30	14.35	24.13	11.25	4.278	5.125
7	Russian	do.	2.45	15.31	21.70	11.44	3.950	5.350
24	do.	Laskowsky.....	3.13	19.48	24.16	10.68	1.800
.....	England	Lawes and Gilbert...	2.50	13.76	15.50	11.25
.....	Germany.....	Mayer.....	2.20	13.75
.....	do.	Wolff.....	2.08	13.00
15	Continental	Millon.....	1.88	11.75	12.63	9.88
12	do.	Peliget.....	2.23	13.97	21.50	9.90
20	do.	Reiset.....	2.04	12.78	17.90	10.68
176	Average, excluding Russia.....	König	1.98	12.35	21.37	7.61
.....	Average of world.....	Kühn	2.11	13.20	24.10	8.20

The average percentage of albuminoids is, for the whole country, lower than for most foreign grain, as has been said, and in no individual case even reaches the amount found in Russian wheat. Whilst among ours the highest percentage occurs in a spring wheat from Dakota, 18.03 per cent., Laskowsky found in a Russian wheat as much as 24.56 per cent., and in twenty-four specimens an average of 19.48 per cent. That the lack of albuminoids in American wheats is not due entirely to enhanced formation of starch is shown by the fact that the weight of one hundred grains of American wheat is no greater, in fact somewhat smaller, than that of foreign specimens.

The variations in the composition of wheat, as well as in the weight per hundred grains, are large. Among our analyses the following extremes are found:

Limits of Variation in the Percentages of the Constituents of Wheats and in Weight per Hundred Grains.

	Highest per cent.	Lowest per cent.	Variation.	Above aver.	Below aver.
Water, . . .	12.49	7.67	4.82	2.33	2.49
Ash, . . .	3.57	.80	2.77	1.65	1.12
Oil, . . .	3.57	1.40	2.53	1.77	.76
Carbohydrates, .	78.66	64.84	13.82	6.68	7.14
Fibre, . . .	3.05	.44	2.61	1.25	1.36
Albuminoids, .	18.03	7.70	10.33	5.88	4.45
Weight of 100 grains,	5.924	1.830	4.094	2.286	1.808

These extremes are in no case due to accidental errors of analyses, as all determinations on which the table is based have been made in duplicate.

The striking feature of the table is that among the important constituents the variation in the albuminoids is the greatest, and the liability to variation in this constituent is a peculiarity of the wheat grain strongly in contrast with maize, as will be seen hereafter. It will be noticed also that the lowest percentages are not as far below as the highest percentages are above the average.

How far these variations are due to the different conditions under which the wheats were grown can be more easily determined by examining the averages for the different sections of the country, which will be seen to depart somewhat from the general average.

The eastern wheat is poorest in ash, albuminoids and size of the

grain. A regular gradation of improvement in this respect takes place from east to west. On the Pacific Coast, however, especially in Oregon, although the size of the grain is very nearly the largest in the country, the albuminoids are the lowest. The question arises how much is due to climate and how much to soil and variety. As regards variety, spring wheats contain much more albuminoid matter than winter grain. They are richer in nitrogen because they have a short period of vegetation and do not, therefore, have an opportunity to store up as much starch. The winter wheats, on the contrary, producing more starch, have a relatively lower percentage of nitrogen but greater weight.

The effect of climate may be very similar; a hot and dry season, of course, shortening the period of growth and hastening the time of ripening. The amount of starch stored in the grain is thus reduced, and the relative percentage of albuminoids increased. This is well illustrated by two wheats from Dakota, one a winter, the other a spring variety, having the following weights per hundred grains and percentages of albuminoids:

	Weight of 100 grains.	Per cent. of albuminoids.
Winter,	3.513	10.68
Spring,	2.755	14.35

If the former were diminished in size and weight, at the expense of its store of starch, it would approach the latter in its relative percentage of albuminoids.

In examining the averages for differences due to climatic causes affecting the accumulation of starch, it is evident that, as our summers are hot and the period of growth consequently short, the albuminoids in American wheat, as a whole, should be higher than that grown in cooler Continental climates. The effect of our hotter and shorter season of ripening does in fact diminish the amount of fibre, and even the size of the grain, but not sufficiently to produce any relative increase in the albuminoids.

In certain parts of the country it has been found that a moist or cool climate has the effect of producing a largely increased formation of starch, and consequent reduction in relative amount of albuminoids and increase in the weight of the grain. I refer to Oregon.

In other local instances the climate has, in conjunction with other conditions of environment, produced a large grain, but the soil and irrigation have been able to furnish supplies of nitrogen sufficient to keep up the relative percentage of albuminoids, or even to raise it above the average. This is the case with Colorado, which will shortly be considered.

As a whole, however, the increase in albuminoids from east to west, followed by an increased weight, denotes that climatic influences are not paramount, and that the changes are due to the soil; the more exhausted soils of the east not being able to furnish such supplies of nitrogenous and ash constituents as the richer ones of the west, the gradual change in composition corresponding to the relative exhaustion of the farming lands.

In Colorado the effect of favorable surroundings, both as regards soil and climate, in producing a fine wheat is well illustrated. The specimens which have been examined were grown on the farm of the Colorado Agricultural College at Fort Collins, by Prof. A. E. Blount. Every care has been taken, both in the selection of the seed, by crossing varieties and by careful cultivation and irrigation, on a new soil particularly adapted to wheat, to obtain a perfect grain. The result has been that the wheats are distinguished by a high percentage of albuminoids, combined with a large weight per hundred grains, thus realising what is most desirable. The albuminoids are not as high as in many spring wheats of the north-west, but their greater size make them of more value by increasing the proportion of flour to bran.

The results have thus far been realised only on an experimental scale, but they serve as well to illustrate the susceptibility of the grain to its surroundings and the possibilities for its improvement.

The analyses extend over three successive years, and the average for each season is given in the following table :

AVERAGE COMPOSITION OF COLORADO WHEAT, CROPS OF 1881, 1882
AND 1883.

	1881.	1882.	1883.
Number of varieties analysed ..	33	12	57
Weight of 100 grains.....grams.....	4.865	4.283	3.941
Waterper cent....	9.86	8.80	9.38
Ashdo ..	2.28	1.99	2.09
Oil.....do	2.41	2.38	} 76.79
Carbohydrates.....do	70.48	72.68	
Crude fibre.....do	1.57	1.76	
Albuminoids.....do	13.40	13.04	11.74
	100.00	100.00	100.00
Nitrogendo	2.14	2.09	1.88

It will be noticed that the crop of 1883 is not equal to those of preceding years, either in weight of the grain or in albuminoids. This is explained by the fact that in June, 1883, when the wheats were in the formation stage, there was a heavy and destructive hail-storm which severely injured the plants. This, occurring at a time when the grain was storing up its albumen, injured it seriously in this respect especially; while the recovery of the plant later resulted in almost the usual increase due to starch and a vigorous growth, encouraged by the moist season which followed. This seems to be sufficient reason for the deficient quality of the crop of 1883.

How differently similar conditions, occurring at other periods of growth, may affect the grain is illustrated by wheat from Ohio grown the same year. These were injured by severe rains just before ripening. The resulting crop was not plump in consequence, and therefore of light weight, owing to its lack of opportunity to fill out the grain with starch. The percentage of albuminoids was, therefore, relatively high, and were the condition of growth unknown, and the size and appearance of the grain unobserved, a mere chemical analysis would be very misleading.

In addition to the generally high average composition of Colorado wheat, as shown by the averages of favorable seasons, we learn much from the study of the individual varieties.

The improvement in seed sent from other localities is marked even in the first crop. For instance, even in the unfavorable season of 1883, eight seed wheats, distributed by the Department of Agriculture, furnished crops which showed a marked improvement, as may be seen by the following comparison:

COMPARISON OF DEPARTMENT SEED AND COLORADO CROPS, 1882-83.

Serial number.	Weight of 100 grains.		Water.		Ash.		Albuminoids.		Nitrogen.	
	Seed.	Crops.	Seed.	Crops.	Seed.	Crops.	Seed.	Crops.	Seed.	Crops.
	Grams.	Grams.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.
2173.....	4.152	...	9.84	...	1.73	...	9.98	..	1.60	...
2174.....	...	4.182	...	9.69	...	2.19	...	11.20	...	1.79
2175.....	3.650	...	9.40	...	1.94	...	11.73	...	1.88	...
2176.....	...	3.650	...	9.50	...	2.10	...	13.65	...	2.18
2177.....	2.820	...	9.74	...	1.94	...	12.60	...	2.02	...
2178.....	...	4.594	...	9.55	...	1.95	...	12.95	...	2.07
2179.....	4.336	...	9.90	...	1.86	...	10.33	...	1.65	...
2180.....	...	4.957	...	10.25	...	2.10	...	12.43	...	1.99
2181.....	2.612	...	11.35	...	1.75	...	12.60	...	2.02	...
2182.....	...	3.231	...	11.11	..	2.04	...	12.60	...	2.02
2183.....	4.084	...	10.50	...	1.95	...	9.80	...	1.57	...
2184.....	...	3.818	...	9.44	...	2.17	...	11.38	...	1.82
2185.....	3.062	...	10.38	...	1.89	...	10.15	...	1.62	...
2186.....	...	2.879	...	9.21	...	2.04	...	10.33	...	1.65
2187.....	3.138	...	9.48	...	2.56	...	16.45	...	2.63	...
2188.....	...	4.064	...	9.92	...	2.20	...	14.53	...	2.32
Average.	3.482	3.922	10.07	9.83	1.95	2.10	11.71	12.38	1.88	1.98
Gain.....	...	6	...	3	...	7	...	7	...	7
Loss.....	...	2	...	5	...	1	...	1	...	1

The crop, as a whole, has improved in ash and albuminoids, and in the size of the grain; while taken individually, there has been a loss in size only twice, and ash and albuminoids in but one variety. Why this has occurred will appear later on.

In the crops of 1881 and 1882 we find the conditions such that the yield after three years' growth has been increased, in some varieties on which observations have been made, to a marvellous extent.

YIELD FROM ONE GRAIN OF DIFFERENT VARIETIES OF WHEAT
INTRODUCED INTO COLORADO.

Variety.	Yield first year.	Yield second year.	Yield third year.
Black Bearded Centennial	203
Judkin.....	320
Australian Club	416
White Fountain.....	440
Russian.....	76	172	448
Touzelles	56	128	480
German Fife	112
Oregon Club	480
Sonora.....	56	110	448
Improved Fife.....	56	126	416
Lost Nation.....	76	96	352
Clawson.....	68	136	544

Selection of the seed, climate, soil, cultivation and irrigation have done this.

Studying the chemical composition and weight of certain varieties in the favorable season of 1882, some interesting facts are discovered.

Twelve selected seed wheats, many of them of very high quality, were sent to the Colorado farm by the Department of Agriculture and the crops returned for analysis. A comparison of the two series is here given.

COMPARISON OF DEPARTMENT SEED AND COLORADO CROP.

Variety.	Water.	Ash.	Oil.	Carbhy- drates.	Fibre.	Albumi- noids.	Weight of 100 grains.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Grams.
McGehee's Red :							
Department.	10.00	1.04	2.46	71.57	1.46	13.47	2.811
Colorado.....	10.00	1.80	1.92	70.85	1.76	13.67	4.159
Finlay :							
Department.	10.00	1.59	2.37	73.22	1.17	11.65	3.285
Colorado.....	10.00	1.83	2.34	71.60	1.72	12.51	4.125
Champ. Amber :							
Department.	10.00	1.88	2.19	73.70	1.33	10.90	3.278
Colorado.....	10.00	2.16	2.42	72.24	1.52	11.66	4.347
Dallas :							
Department.	10.00	2.10	2.43	71.54	1.61	12.32	4.023
Colorado.....	10.00	1.85	2.46	69.34	1.73	14.52	4.610
Bennett :							
Department.	10.00	2.01	2.17	70.77	1.35	13.70	3.218
Colorado.....	10.00	2.15	2.52	70.00	2.00	13.33	3.976
Lemon :							
Department.	10.00	1.87	2.46	68.87	1.50	15.30	3.417
Colorado.....	10.00	2.02	2.10	72.01	1.65	12.22	4.335
Gold Medal :							
Department.	10.00	1.77	2.33	74.89	1.36	9.65	3.076
Colorado.....	10.00	1.78	2.24	72.11	1.72	12.15	4.374
German Amber :							
Department.	10.00	1.66	2.57	74.01	1.02	10.74	2.938
Colorado.....	10.00	1.77	2.39	71.84	1.73	12.27	4.027
Rice :							
Department.	10.00	2.11	2.28	69.73	1.60	14.28	3.586
Colorado.....	10.00	2.06	2.35	69.70	1.94	13.95	4.103
Wash'ton Glass :							
Department.	10.00	2.02	2.19	72.20	1.81	11.88	3.741
Colorado.....	10.00	1.92	2.37	73.16	1.16	11.39	4.450
Swamp :							
Department.	10.00	2.04	2.01	68.05	1.79	16.11	3.660
Colorado.....	10.00	2.05	2.30	68.89	1.85	14.91	4.423
Wysor :							
Department.	10.00	1.54	2.14	72.11	1.72	12.49	3.796
Colorado.....	10.00	2.22	2.16	71.13	2.09	12.40	4.609
Average Seed :							
Department.	10.00	1.80	2.30	71.72	1.47	12.75	3.402
Colorado.....	10.00	1.97	2.30	71.07	1.74	12.92	4.299
Gain for crop.....	9	7	9	11	6	12
Loss.	3	5	3	1	6	0

The average composition of the seed wheats is, to begin with, as has been said, good, and many of them are high in albuminoids. The weights of one hundred grains are, however, rather low. The average for the crop shows a slight gain in ash, no change in oil, a gain in fibre and a small rise in albuminoids.

The gain in ash is due to richer soil, that in fibre to the longer vegetative period ; but the question arises why there has not been a greater gain in albuminoids ? This can be explained by a study of the individual analyses. It has been shown that the average amount of albuminoids in the whole crop of 1882 was about 13 per cent., and it will be seen that those that were from seed containing higher percentages than this fell toward it, while those lower in amount rose ; that is to say, six increased and six diminished in the amount of albuminoids they contained. This seems to point to the fact that in the season of 1882 the conditions were such that the soil of Colorado was able to produce a wheat containing about thirteen per cent. of albuminoids, and that if the seed sown contained more than this, there was a tendency toward a decrease in amount, and the reverse. Reversion, apparently, takes place more easily than improvement.

In considering this point, regard must be had for the fact that, while the relative amounts of albuminoids average the same in both seed and crop, they are not absolutely the same, because there has been a large increase in the size of the grain, in fact over twenty-five per cent. There must have been, consequently, an absolute increase of the same amount of nitrogenous substance in order to preserve the same ratio.

That the quality of the seed has an effect on the crops is made apparent by a division of the analyses of the crops of 1882 into certain classes, as has been done in the next table, according to the source of the seed.

Colorado Crops of 1882.

	All.	Averages of		Domestic.
		Russian.	Foreign.	
33 Varieties.				
Weight of 100 grains,	4.865	5.075	5.187	4.714
Water,	9.86	9.69	9.86	9.85
Ash,	2.28	2.41	2.32	2.27
Oil,	2.41	2.44	2.45	2.38
Carbohydrates, . .	70.48	69.49	69.46	70.87
Crude fibre, . .	1.57	1.59	1.57	1.58
Albuminoids, . .	13.40	14.54	14.34	13.05

The Russian seeds were of the best quality, and the crops correspond. The domestic seeds were of poor quality, and the crops correspondingly low.

The conditions in Colorado do not seem to permit the production, for any length of time, of a grain containing, as the Russian varieties do, more than 13 per cent. Reversion begins at once in grains having a higher amount. Nos. 2187 and 2188, analyses of which are given in a preceding table, illustrate this, 2187 being a Russian spring wheat with 16.45 per cent. of albuminoids, and the crop from it, 2188, having 14.53 per cent. Another year 2188 would probably fall still lower, but not quite as low as the usual average of 13 per cent.

Analyses of the grain of 1884 have not yet been made, but they will undoubtedly furnish some results of interest.

In concluding the subject of wheat, attention must be called to the recent experiments, published in the Journal of the Chemical Society,¹ by Lawes and Gilbert. Their results, derived from the analyses of 92 specimens of wheat grain and wheat straw, in which the ash constituents and nitrogen were determined, and which were grown under the most varied conditions of soil and season, agree in many respects with our conclusions derived from Ohio, Minnesota, Dakota, Colorado and Oregon grain.

Maize.

Analyses of maize, about two hundred in number, have furnished the basis for the following averages:

AVERAGE COMPOSITION OF AMERICAN CORN.

Locality.	Ash.	Albumi- noids.	Nitrogen.	Number of analyses.	Lowest albumi- noids.	Highest albumi- noids.
	Per cent.	Per cent.	Per cent.		Per cent.	Per cent.
America, 1882	1.52	10.46	1.67	114	7.00	13.05
America, 1883	1.58	10.31	1.65	88	7.88	12.63
Average	1.55	10.39	1.66	202	7.00	13.65
New York	1.43	10.54	1.69	9	9.10	12.43
Illinois	1.48	10.06	1.61	20	7.88	12.08
Minnesota ,	1.68	10.07	1.61	16	8.40	12.43
Dakota ..	1.57	10.75	1.72	15	9.28	12.25
Nebraska	1.54	10.47	1.68	13	9.10	12.25
Colorado	2.23	9.89	1.58	4	8.93	12.25
California	1.56	10.26	1.64	11	8.40	11.73

¹ Jour. Chem. Soc. 1884, 45, August.

A part of these, 114 in number, have been examined in greater detail, and from them other averages have been deduced.

AVERAGE COMPOSITION OF AMERICAN CORN (MAIZE).

Locality.	Weight of 100 kernels.	Water.	Ash.	Oil.	Carbohydrates.	Fibre.	Albuminoids.	Nitrogen.	Weight of largest 100 kernels.	Weight of smallest 100 kernels.	Highest albuminoids.	Lowest albuminoids.	No. of analyses.	No. of weights of 100 kernels.	Analyst.
		Pr. ct.	Pr. ct.	Pr. ct.	Pr. ct.	Pr. ct.	Pr. ct.	Pr. ct.	Grams.	Grams.	Pr. ct.	Pr. ct.			
America.....	36,910	10.04	1.52	5.20	70.69	2.09	10.46	1.67	52,679	23,605	13.65	7.00	114	61	
Northern States.....	37,320	8.96	1.54	5.11	71.32	1.41	10.64	1.70	44,147	30,610	13.65	7.53	30	3	
South.....	9.08	1.37	4.94	72.06	1.72	10.95	1.75	11.03	10.88	2	...	
Middle West.....	32,457	12.33	1.43	4.97	68.16	2.22	10.89	1.70	12.00	9.20	15	1	
Far West.....	37,528	9.50	1.55	5.30	70.75	2.47	10.43	1.67	52,679	28,348	12.78	8.23	53	53	
Pacific Slope.....	27,900	9.78	1.48	9.40	72.13	2.67	8.14	1.30	8.40	7.88	2	1	
Mexico.....	9.58	1.58	5.48	71.34	1.68	10.34	1.65	10.67	10.15	3	...	
New Hampshire.....	10.10	1.58	5.48	70.15	1.11	11.07	1.85	13.65	10.50	11	...	Department of Agriculture.
Vermont.....	8.64	1.45	5.63	72.76	1.38	10.14	1.62	1	...	do.
Connecticut.....	10.84	1.54	4.70	70.98	1.46	10.48	1.69	11.63	9.19	13	...	S. W. Johnson, W. O. Atwater.
Pennsylvania.....	37,320	7.96	1.43	5.22	74.54	1.97	8.88	1.42	44,147	30,610	10.15	7.53	5	3	Department of Agriculture.
North Carolina.....	8.96	1.37	4.94	72.06	1.72	10.95	1.75	11.03	10.88	2	...	Johnson and Department.
Kentucky.....	32,457	7.70	1.50	5.33	73.47	2.20	9.80	1.57	1	...	Department of Agriculture.
Tennessee.....	7.58	1.23	5.09	74.16	2.65	9.29	1.48	1	...	do.
Indiana.....	11.29	1.28	4.87	70.16	1.90	10.16	1.68	1	...	R. C. Kedzie.
Michigan.....	13.20	1.45	4.95	67.05	2.21	11.14	1.73	12.00	9.88	12	...	do.
Missouri.....	38,411	8.18	1.68	5.28	72.00	2.33	10.54	1.68	52,679	30,674	12.78	8.23	26	26	Department of Agriculture.
Kansas.....	33,271	11.94	1.49	4.87	69.39	2.16	10.15	1.62	36,687	28,348	10.68	9.10	6	6	do.
Colorado.....	34,120	10.50	1.50	5.66	70.19	2.35	9.80	1.60	1	1	do.
Texas.....	37,833	10.44	1.42	5.45	69.52	2.77	10.40	1.66	43,799	30,898	11.03	9.80	20	20	do.
Oregon.....	9.25	1.46	7.08	73.07	1.26	7.88	1.26	1	...	do.
Wash. Territory.....	27,900	10.30	1.50	5.73	71.19	2.88	8.40	1.34	1	...	do.
Mexico.....	9.58	1.58	5.48	71.34	1.68	10.34	1.65	10.67	10.15	3	...	do.

In comparison with the averages of other investigators on the Continent, there will be seen to be a much greater degree of agreement than was the case with wheat.

AVERAGE OF AMERICAN CORN COMPARED WITH AVERAGES OF FOREIGN INVESTIGATIONS.

Constituent.	Richardson.	Koenig.	Wolff.
Water	10.04	13.12	14.40
Ash	1.52	1.51	1.50
Oil	5.20	4.62	6.50
Carbohydrates	70.69	68.41	62.10
Fibre.....	2.09	2.49	5.50
Albuminoids	10.46	9.85	10.00
	100.00	100.00	100.00
Nitrogen	1.67	1.58	1.60
Number of analyses ..	114	145	...

A study of the extremes in the percentages of the various constituents given in the next table shows that the variations are within smaller limits in maize than in wheat, at least for most of them.

VARIATIONS OR EXTREMES FOR EACH CONSTITUENT OF CORN.

Constituent.	Highest percentage.	Lowest percentage.	Variation.	Above average.	Below average.
Water.....	15.10	7.40	7.70	5.06	3.64
Ash	3.08	1.03	2.05	1.53	.55
Oil.....	7.49	3.92	3.57	2.29	1.28
Carbohydrates.....	75.73	65.97	9.76	5.04	4.72
Fibre.....	3.10	.78	2.32	1.01	1.31
Albuminoids.....	13.65	7.00	6.65	3.19	3.46
Weight of 100 kernels, grams..	53.679	23.605	29.074	15.769	13.305

The variations are somewhat larger in moisture in maize, but the albuminoids never reach the high percentages at times found in wheat. Maize is influenced by the same causes as wheat, but its longer vegetative period renders it more independent of its environment, at least as far as the composition of the grain is concerned. The averages for different parts of the country are more nearly alike. In some cases, where the analyses are few in number, the averages are low, but excluding these, since they are hardly representative, the remainder vary but slightly. The few specimens

from the Pacific Coast, like the wheats from that locality, are poor in albuminoids. This may be due to the same climatic causes, but the average weight per hundred kernels is not above that of the rest of the country, and, therefore, the poverty in nitrogen can hardly be attributed to enhanced starch formation. The size of the kernel of maize, in fact, does not seem to influence its composition as it does in the case of wheat. In the original report upon this subject the weights of a thousand specimens from all parts of the country show the extremes of size to be very wide apart, viz. 64.102 and 13.858 grams per hundred, and yet the following analyses of certain specimens, selected at each extreme, show that, while the largest kernels seem to have made their increase in size somewhat at the expense of the albuminoids, and the smallest to be slightly richer in nitrogen from lack of starch in the kernel, the difference between the two kinds, large and small, is not as great as might be expected from our previous experience with wheat, for in each group we find a grain having the same percentage of albuminoids, 9.45. The longer vegetative period and the stronger roots must be the explanation of these facts in regard to maize.

ANALYSES OF THE LARGEST AND SMALLEST KERNELS OF MAIZE
SELECTED FROM 1000 SPECIMENS.

Weight of 100 kernels.	Albuminoids.
61.141	8.58
64.102	9.63
63.384	9.45
60.909	8.58
Average, largest, 62.359	9.09
18.698	11.90
22.091	9.45
19.982	10.33
16.073	10.33
Average, smallest, 19.211	10.50

It is my intention to extend this investigation to the other cereals, oats, barley and rye, and to continue the collection of data in regard to wheat and maize. In conclusion, I desire to call attention to a typographical error in the table on page 29 of Bulletin No. 4. The average albuminoids for the United States and Provinces should read 12.53 instead of 10.53.

Contributions from the Sheffield Laboratory of Yale College.

XXI.—ON THE RELATIVE DIGESTIBILITY OF FISH FLESH IN GASTRIC JUICE.

BY R. H. CHITTENDEN AND GEO. W. CUMMINS.

The value of food as nutriment depends primarily upon the presence in suitable quantity of elements, or combination of elements, capable of supplying the needs of the body; coupled with this, however, is the ease with which the food stuff in question can be rendered available by the system for its wants. This, or in other words its *digestibility*, constitutes a very important item in determining the true nutritive value of any food. If, of two foods possessing a like chemical composition, one be more easily digestible, that one, though containing no more available nutriment than the other, is in virtue of its easier digestibility more valuable as a food stuff and in one sense more nutritious, as well as more economical for the system.

Both chemists and physiologists have appreciated the importance of all data relative to the nutritive value of foods. But hitherto nearly all work in this direction has been confined to a study of chemical composition, and only occasionally to digestibility. The mere fact, however, that a substance contains a certain percentage of nitrogen is not alone sufficient. We need to know in addition, not only how much of the nitrogen passes through the body unabsorbed, thus indicating how much is ordinarily available for nutriment, but we need to know likewise how long the food stuff remains in the stomach, how quickly it is acted upon by the digestive juices, and, finally, how much passes out undigested; points of great importance to the healthy system, but still more so to the system weakened by disease.

There are two ways of determining the digestibility of a food stuff in gastric juice. One consists in the introduction of a weighed amount of the substance into the stomach of a man or animal through a fistulous opening, and noting the length of time required for its solution; the other, in the use of an artificial gastric juice by which the amount of substance capable of being dissolved and digested in a given time can be quantitatively ascertained. The

first of these methods was made use of by Dr. Beaumont in his celebrated experiments on the Canadian, Alexis St. Martin, about 1830, and has been employed many times since with animals by other workers. While it would appear in some respects to be the better method, there are reasons why it is not so advantageous as the other, mainly because it is not capable of showing such small differences, it is not free from nervous influences and personal idiosyncrasies, and, lastly, it is less convenient. The method with artificial gastric juice, on the other hand, admits of the conditions being the same in each case, and since the digestion of a food is by itself simply a chemical process, it would seem better in a determination of *digestibility* that the process be shorn of all those conditions, natural or otherwise, which tend to interfere with the purely chemical action of the digestive juice.

Few experiments appear to have been made on the digestibility of fish; this is the more strange when we consider what an important item of food fish constitutes, particularly along our seaboard. Yet the idea is prevalent, based apparently on general grounds, that fish flesh is not easily digestible. Thus Maly¹ mentions that "fish flesh is difficult of digestion, although the reason is not known." Still, as Voit² remarks, "nothing certain is known regarding the digestibility of different kinds of flesh, although much is said concerning it. Probably digestibility is in part dependent upon the nature of the fat present and the manner of its distribution; thus the presence of a difficultly fusible fat with considerable stearin would tend to hinder digestibility (as in mutton); the same thing probably occurs when the contents of the sarcolemma are permeated with much fat (as in the lobster and eel.)" This statement at once suggests the probability of great variation in the digestibility of the flesh of any one species, dependent on a large number of conditions, which, in the case of fish particularly, are somewhat difficult of control; thus age, sex, food, period of spawning, length of time they have been preserved, are a few of the many natural conditions which would tend to modify the digestibility of the flesh and render generalisations from even a large number of results somewhat uncertain.

Still, as no systematic experiments appear ever to have been tried with fish flesh, we have attempted to obtain some positive results concerning the relative digestibility of the more common

¹ Hermann's Handbuch der Physiologie 5, 112.

² *Ibid.* 6, 447.

edible species, as well as the general digestibility of fish as compared with beef, veal, lamb, etc.

The Method Employed.

The gastric juice.—For reasons already given, artificial digestion was chosen as the best adapted for the purpose, and with this end in view a gastric juice was needed which should be both constant in composition and activity during the length of time required for trying the experiments. A large quantity of so-called "pure pepsin"¹ was obtained, thoroughly sampled, and then placed in a tightly stoppered bottle and kept in a cool, dry place to prevent change. The acid used was pure hydrochloric of exactly 0.2 per cent. strength. From this material fresh gastric juice was made for each series of experiments, 5 grams of the pepsin being dissolved in 1 litre of the dilute acid. This furnished a digestive mixture of suitable strength, and, as subsequent experiments showed, well adapted to the purpose.

Preparation of the flesh.—In order that a fair sample of the flesh might be obtained in each case, 100 grams, freed from tendons, fat, skin and bones, were weighed off and finely divided by chopping. Small portions of the sample tissue were then taken for a determination of the amount of solid matter,² and then two portions of 20 grams each were weighed out to determine the digestibility. These two latter portions were placed in small porcelain mortars covered with watch glasses, and then set into a steam-bath heated by a large gas flame for 30 minutes. This bath was a small copper oven, on the bottom of which was a layer of water 1 or 2 inches in depth, while some distance above this was placed a perforated plate upon which the dishes were set, the whole provided with a tightly fitting cover, with a small outlet for the escaping steam. Heated in this for half an hour the fish or meat was thoroughly and evenly cooked without loss of any extractives, and being in mortars, the tissue after steaming could be ground up fine without loss. The flesh was then ready for digestion.

The digestion.—As already stated, two separate or duplicate determinations were made of each sample. Each portion of 20 grams was placed in a beaker with 200 cc. of the standard gastric juice, covered with a watch glass and set into a bath heated at 38–40° C.

¹ Manufactured by Henry Thayer & Co.

² Determined by simply drying at 100° C. until of constant weight.

for 22 hours with occasional stirring. This bath consisted of a metal box with a movable cover, and having about midway of its height a perforated plate upon which the beakers were placed. The bath was filled with water to such an extent that the beakers were immersed about half an inch. The space above, when the bath was closed, was of course saturated with aqueous vapor, and thus any evaporation of the contents of the beakers was prevented. The temperature was kept quite constant by a small gas flame, and the extreme variations were not more than $35-42^{\circ}$ C., these occurring only during the night and early morning. The length of time the mixtures were heated, viz. 22 hours, was no longer than was necessary to insure accurate and concordant results. In an artificial digestion the accumulation of the products formed tends to retard the action of the fluid, but in no case were our results impaired by saturation of the digestive mixture, for that this could never have occurred ordinarily is plainly shown by the large amount of *blood fibrin* dissolved by the gastric juice in a trial experiment. The addition of larger amounts of flesh, moreover, in the case of fish, 30-40 grams, simply diminished the digestive action.

Determination of the amount digested.—This can be accomplished by either weighing the undigested residue, or by determining directly the amount dissolved. In a recent work by Jessen¹ on the influence of different modes of preparation on the digestibility of meat, the former method was used. Unless the amount of water contained in the meat experimented with, however, is determined, a very decided error may be introduced. Thus Jessen found by experiment with frogs' legs² that 2 grams of the raw flesh, introduced into the stomach of a dog, required on an average 4.46 hours for digestion, while the same amount of beef, similarly prepared, required on an average 5.58 hours, and thus from this experiment the relative digestibility of the two would be as 84 : 100. Our experiments, however, show quite a different result, easily explained by a determination of the percentage amount of solid matter in the two kinds of flesh. Thus, while 20 grams of beef contain on an average 5.1 grams of solid matter, the flesh of frogs' legs contains but 3.5 grams. It is evident from this example, then, that a determination of the total solid matter is necessary in each species of flesh; but even when that is done, and corrections made

¹ Zeitschrift für Biologie 19, 130.

² *Ibid.* p. 140.

accordingly, we have found a decided difficulty in filtering the digestive mixtures. The undissolved residue of the fish is so gelatinous that it is next to an impossibility to wash it entirely free from peptones. We, therefore, decided to work with the filtrate, and after several trials by precipitating the dissolved albumin with tannic acid, according to the method of Johnson,¹ and also by determining the specific gravity of the fluid after filtration, we finally adopted the following method, which has proved quite satisfactory. After the gastric juice has been allowed to act for the requisite length of time on the 20 grams of flesh the mixture is cooled to 20° C., and then diluted to 250 cc., in a graduated flask, with distilled water. After being thoroughly mixed it is filtered on a dry filter, and then 50 cc. or one-fifth of the entire mixture, is transferred by a pipette to a small weighed dish, and to it are added 5 cc. of a standard solution of sodium carbonate of such strength as exactly to neutralise the acid present. The fluid is then evaporated to dryness on the water-bath, and finally dried at 110° C. until of constant weight. In order that the results obtained may express the absolute amounts of matter dissolved by the gastric juice, it is necessary to carry on control experiments with the gastric juice itself. This is also desirable as a proof of the uniform strength of the gastric juice. Thus in each series of experiments 200 cc. of the standard juice were warmed at 38–40° C. for 22 hours, so that all albumin contained in the pepsin could be converted into peptone, then diluted to 250 cc. and 50 cc., neutralised, evaporated, and dried as already described. This residue, subtracted from the weight of the residue left by the evaporation of the 50 cc. of the digestive mixtures, multiplied by 5, gives quite accurately the amount of matter (peptones and intermediate products together with some salts) dissolved from the 20 grams of flesh. Theoretically there are one or two minor objections to this method, the most noticeable, perhaps, being the variable amount of undigested residue suspended in the fluid diluted to 250 cc. The amount of space, however, occupied by this matter is not large, and its influence on the accuracy of the method not great. Again, by the evaporation of the peptones, and drying at 110° C., there is doubtless some slight oxidation, but still it cannot be great, as the dried residue is soon brought to a constant weight. While the method seems longer than to weigh the undissolved residue, it is by far more accurate, and in the end we believe shorter.

¹ Bulletin de la Société chimique de Paris **23**, 40.

The fish experimented¹ with were obtained at a local market, and while always quite fresh and in good condition, we had no means of knowing how long they had been out of water.

In all of the experiments the flesh was cooked by steaming, unless otherwise expressed.

Tables I-V give all the data of the experiments, while table VI contains the average amounts digested of each sample of cooked flesh, together with the relative digestibility as compared with cooked (steamed) beef, taken as 100.

A glance at the results of the control analyses of the gastric juice alone plainly shows the constancy of its composition. The strength and activity of the digestive mixture, moreover, is easily seen from the amount of blood fibrin (Table IV) dissolved by 200 cc. of the fluid; an amount far in excess of the fish or beef dissolved by the same quantity of fluid.

The results of the analyses show plainly that the method adopted is as good as could be expected, for it must be remembered that the two results obtained from each sample of flesh are not merely from duplicated analyses, but from duplicated digestions as well, and in these, extending as they do over 22 hours, with slight variations in temperature and agitation, small differences are to be expected. The very great divergence noticed, however, in the results obtained from *different* samples of the same species of flesh show at once that there are other conditions, such as age, etc., which affect the digestibility of the flesh more or less, so that, in order to obtain results from which to draw strict generalisations, it would be necessary to experiment with fish of different species, of like age, sex, and reared under like conditions. As examples of this we have the very divergent results from two samples of veal, and also of two blue fish (88.69 and 73.44). As direct evidence that age, sex, etc., do exert a modifying influence on the digestibility of flesh, we have three experiments on the flesh of the lobster; one with a small young lobster, a second with a large female, and a third with a large male of the same species. The duplicate digestions gave fairly concordant results; the average relative digestibility being for the young specimen 87.81, for the large female 79.06, and for the male 69.13. This shows plainly some modifying influence in the flesh itself. In composition, so far as the solid matter is con-

¹For composition of the fish experimented with, see "Zur Chemie der Fische," Berichte der deutsch. chem. Gesell. **16**, 1839, by Prof. W. O. Atwater.

TABLE I.

	FIRST SERIES. April 18.		SECOND SERIES. April 21.		THIRD SERIES. April 23.		FOURTH SERIES. April 25.		FIFTH SERIES. April 28.	
	Hippoglossus vulgaris, Halibut.	Hiatula onitis, Tautog.	Salvelinus fontinalis, Brook Trout.	Scomber scombrus, Mackerel.	Esox lucius, Pike.	Roccus americanus, White Perch.	Pluronectidae Americanus, Flat Fish.	Perca Americana, Yellow Perch.	Roccus lineatus, Striped Bass.	Salmo salar, Salmon.
Grams taken.....	<i>a</i>	<i>b</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>b</i>
Gave dried residue.....	5.8010 5.1408	6.6509 .4162	4.9927 5.4913	4.6668 5.0266	7.3142 4.8280	6.0013 6.1071	6.4609 7.2258	7.7409 8.3051	7.4441 7.2179	8.9733 9.5412
Per cent. solid matter.....	1.1857 1.0350	1.3703 1.3102	.9634 1.0703	1.1755 1.5316	1.4381 .9467	1.3497 1.2236	1.1031 1.2445	1.4029 1.5069	1.5497 1.4924	2.8687 2.9580
	20.43 20.13	20.60 20.60	19.49 19.07	25.18 25.84	19.66 19.61	19.55 19.74	17.09 17.22	18.10 18.14	20.81 20.60	32.00 31.00
Average per cent. solid matter.....	20.28	20.60	19.58	25.51	19.635	19.695	17.155	18.12	20.735	31.50
20 gr. sampled flesh and 200 cc. S. G. J. 22 hrs. at 40°—diluted to 250 cc. 50 cc. of this + 5 cc. Na ₂ CO ₃ gave dried residue.....	<i>a</i>	<i>b</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>a</i>	<i>b</i>	<i>b</i>
	1.0070 1.0134	1.0223 1.0401	lost.	1.0201 1.0113	.9139 1.0540	.9102 .8950	.8437 .8641	.8962 .8905	.9612 .9764	1.0596 1.0206
200 cc. S. G. juice diluted to 250 cc. 50 cc. of this + 5 cc. Na ₂ CO ₃ gave dried residue.....	0.3180		0.3178		0.3123		0.3126		0.3134	
Residue from digestion less the gas- tric juice residue.....	.6890 .6954	.7043 .72216349 .7023	.6016 .7417	.5979 .5827	.5311 .5515	.5836 .5779	.6478 .6630	.7462 .7072
The above X 5 or the entire products of digestion from 20 gr.....	3.4450 3.4750	3.5215 3.6105	3.1745 3.5115	3.0080 3.7085	2.9895 2.9135	2.6555 2.7575	2.9180 2.8805	3.2390 3.3150	3.7310 3.5560
Average of the above.....	3.4000	3.5060	3.1745	3.4895	3.35825	2.9515	2.7065	2.9037	3.2770	3.6335

TABLE II.

	SIXTH SERIES, April 30.		SEVENTH SERIES, May 2.		EIGHTH SERIES, May 5.		NINTH SERIES, May 5.		TENTH SERIES, May 12.	
	Sparus chrysops, Porgie.	Clupea sapidissima, Shad.	Latjanus Blackfordi, Red Snapper.	Anguilla rostrata, Bel.	Beef.	Veal.	Gadus aeglefinus, Haddock.	Paralichthys dentatus, Flounder.	Bothus maculatus, Day Light.	Prionotus palmipes, Sea Robin.
	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
Grams taken.....	7.6491	6.9103	8.2403	7.9472	5.4109	6.7188	6.2437	5.7730	6.6987	4.7103
Gave dried residue.....	1.7221	1.5047	2.6035	2.4791	1.3093	1.7681	1.5607	1.1395	1.2301	.8670
Per cent. solid matter.....	22.51	22.61	31.57	31.11	25.79	26.31	24.99	21.93	18.37	18.38
Average per cent. solid matter.....	22.56	31.335	22.095	21.785	26.035	24.96	18.245	23.045	18.375	21.87
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
20 gr. sampled flesh and 200 cc. S.C.J., 22 hrs. at 45°—diluted to 250 cc. 50 cc. of this + 5 cc. Na ₂ CO ₃ gave dried residue.....	1.0081	1.0215	1.0538	1.0254	1.1404	1.1355	1.1553	1.1436	.8949	.8904
200 cc. standard gastric juice diluted to 250 cc. 50 cc. of this + 5 cc. Na ₂ CO ₃ gave dried residue.....										
Residue from digestion less the gas- tric juice residue.....	.6976	.7110	.7433	.7149	.8258	.8209	.8407	.8290	.5808	.5763
The above X 5 or the entire products of digestion from 20 gr.....	3.4880	3.5550	3.7165	3.5745	4.1290	4.1045	4.2035	4.1450	2.9040	2.8815
Average of the above.....	3.5215	3.6455	3.3040	2.9062	4.1107	4.1742	3.3382	3.4525	2.8927	3.1572

TABLE III.

	ELEVENTH SERIES. May 14.				TWELFTH SERIES. May 19.				THIRTEENTH SERIES. May 19.				FOURTEENTH SERIES. May 22.				FIFTEENTH SERIES. June 2.			
	Salmo salar. Salmon.	Gadus calla- rias. Cod.	Coregonus clupeiformis. Lake White.	Homarus Americanus. Lobster. Young.	Crab.	Pomatopus salinator. Blue Fish.	Cynoscion regale. Weak Fish.	Veal.	Clupea harengus. Herring.	Stromateus triacanthus. Butter Fish.										
Grams taken.....	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b				
Gave dried residue.....	4.3470	4.8259	5.5381	5.8743	6.3449	4.9515	3.3703	2.8816	5.1634	5.0654	6.6347	5.6029	5.4457	4.4405	5.5057	4.7300				
Per cent. solid matter.....	1.3383	1.1104	1.0684	1.0684	1.6253	1.2639	7.300	.6297	1.2195	1.1922	1.2901	1.1109	1.3332	1.0719	1.3483	1.1500				
	30.81	31.31	18.40	18.13	25.61	25.52	21.66	21.85	23.61	23.53	19.42	19.51	24.48	24.10	24.47	24.52				
Average per cent. solid matter.....	31.06	18.29	25.565	21.755	23.57	19.465	19.785	24.29	24.495		24.495		22.89		22.97	22.81				
20 gr. sampled flesh and 200 cc. S.G.J. 22 hrs. at 40°—diluted to 250 cc. 50 cc. of this + 5 cc. Na ₂ CO ₃ gave dried residue.....	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b				
	1.0663	1.0495	.8922	.9015	1.0826	1.0842	1.0153	1.0388	.8621	.8591	.8712	.9421	.9090	lost.	.9780	.9811				
200 cc. standard gastric juice 22 hrs. at 40°—diluted to 250 cc. 50 cc. of this + 5 cc. Na ₂ CO ₃ gave dried residue.....	0.3110				0.3164				0.3123				0.3154				0.3137			
Residue from digestion less the gastric juice residue.....	.7553	.7385	.5812	.5905	.7662	.7678	.6989	.7224	.5498	.5368	.5589	.6298	.58366978	.7143				
The above X 5 or the entire products of digestion from 20 gr.....	3.7765	3.6925	2.9060	2.9525	3.8310	3.8390	3.4945	3.6120	2.7490	2.6840	2.7945	3.1490	2.9180	3.4890	3.5215				
Average of the above.....	3.7345	2.9292	3.8350	3.5532	2.7165	2.9717	2.9180	3.5052	3.3317		3.3317		3.5052		3.3317					

TABLE IV.

	SIXTEENTH SERIES. May 7.				SEVENTEENTH SERIES. June 2.				EIGHTEENTH SERIES. June 2.				NINETEENTH SERIES. June 3.				TWENTIETH SERIES. June 16.			
	Serramis atrarius. Sea Bass.		Serramis atrarius. Sea Bass		Beef.		Beef.		Clupea sapi- dissima. Shad. Dark meat.		Clupea sapi- dissima. Shad. White meat.		Beef.		Beef.		Lobster. Large Male.		Blood Fibrin.	
	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b		
Grams taken	5.2485	6.0050	5.8633	5.7788	4.0414	4.4600	6.6883	5.1362	4.6522	5.0094	4.6161	5.1282
Gave dried residue.....	1.1153	1.2872	1.4781	1.4471	1.3118	1.4640	2.0627	1.5359	1.2089	1.28429643	1.0610
Per cent, solid matter.....	21.24	21.10	25.20	25.04	32.46	32.81	30.84	29.93	25.75	25.63	20.89	20.64
Average per cent. solid matter.....	21.17	21.17	25.12	25.12	32.63	32.63	30.38	30.38	25.69	25.69	20.76	20.76
	20 gr.	20 gr.	30 gr.	40 gr.	20 gr.	20 gr.	30 gr.	raw.	20 gr.	20 gr.	20 gr.	20 gr.	20 gr.	20 gr.	raw.	20 gr.	20 gr.	20 gr.	indef.	quant.
Sampled flesh and 200 cc. S.G.J. 22 hrs. at 40°—diluted to 250 cc. 50 cc. of this + 5 cc. Na ₂ CO ₃ gave dried residue.....	.9919	.9999	.9625	.8200	1.1476	1.1493	1.1920	1.4685	1.0290	1.0225	1.1156	1.0867	1.1329	1.1244	1.0668	1.1032	.8325	.9141	1.9238
200 cc. standard gastric juice diluted to 250 cc. 50 cc. of this + 5 cc. Na ₂ CO ₃ gave dried residue.....	0.3160				0.3163				0.3141				0.3128				0.3141			
Residue from digestion less gastric juice residue.....	.6759	.6839	.6465	.5040	.8313	.8330	.8757	1.1522	.7049	.7081	.8015	.7726	.8201	.8116	.7540	.7904	.5184	.6000	1.6097
The above X 5 or the entire products of digestion from 20 gr.....	3.3795	3.4195	3.2325	2.5200	4.1595	4.1650	4.3785	5.7610	3.5245	3.5420	4.0075	3.8630	4.1005	4.0580	3.7700	3.9520	2.5920	3.0000	8.0485
Average of the above.....	3.3995	3.2325	2.5200	4.1607	4.3785	5.7610	3.5332	3.5332	3.9352	4.0792	3.8610	2.7960	8.0485

TABLE V.

	TWENTY-FIRST SERIES. June 4.			TWENTY-SECOND SERIES. June 9.			TWENTY-THIRD SERIES. June 16.			TWENTY-FOURTH SERIES. June 18.		
	Lamb.		Mutton.	Pomatomus saltator. Blue Fish.		Pomatomus saltator. Blue Fish.	Light meat of Spring Chicken.		Dark meat of Spring Chicken.	Frog Legs.		Lobster. Large female.
	a	b		a	b		a	b		a	b	
Grams taken.....	4.428	5.1652	5.2508	5.1936	5.8776	4.7043	4.6394	4.3887	5.1115	3.6942	4.3595
Gave dried residue.....	1.3533	1.5272	1.6352	1.0328	1.1639	1.2516	1.2384	1.1585	.9105	.6618	.9236
Per cent. solid matter.....	30.18	29.56	31.14	19.38	19.80	26.60	26.69	26.39	17.81	17.91	21.19
Average per cent. solid matter.....	29.87		30.84	19.84		19.84	26.645		26.79	17.86		21.29
20 gr. sampled flesh and 200 cc. S. G. J. 22 hrs. at 40°—diluted to 250 cc.	a	b	a	a	b	a	a	b	a	b	a	b
50 cc. of this + 5 cc. Na ₂ CO ₃ gave dried residue.....	1.0313	1.0201	1.0753	1.0632	1.0713	1.0412	1.0308	1.0010	.9991	.9724	.9611	.9575
200 cc. standard gastric juice diluted to 250 cc.												
50 cc. of this + 5 cc. Na ₂ CO ₃ gave dried residue.....												
Residue from digestion less the gastric juice residue.....	.7172	.7060	.7612	.7483	.7564	.7264	.7167	.6879	.6850	.6564	.6451	.6381
The above X 5 or the entire products of digestion from 20 gr.....	3.5860	3.5300	3.8060	3.7415	3.7820	3.6320	3.5835	3.4345	3.4250	3.2850	3.2250	3.1955
Average of the above.....	3.5580		3.7287	3.7617		3.5885	3.5090		3.4160	3.2535		3.1990

TABLE VI.

Average results from each sample of cooked flesh.

	Percentage solid matter.	Solid matter in 20 grams.	Average amount digested from 20 grams.	Relation of the amounts digested to the amount digested from 20 grams cooked beef = 4.0491.
Beef.....	25.12	5.024	4.1607	} = 100.00
Beef.....	26.03	5.206	4.1167	
Beef.....	25.69	5.138	3.8610	
Veal.....	24.96	4.992	4.1742	} = 94.89
Veal.....	24.29	4.858	3.5952	
Mutton.....	30.84	6.168	3.7287	
Lamb.....	29.87	5.974	3.5580	92.15
Spring chicken (light meat).....	26.64	5.328	3.5990	87.93
“ (dark meat).....	26.70	5.340	3.4160	86.72
Lake White (<i>Coregonus clupeiformis</i>).....	25.56	5.112	3.8350	84.42
Shad (<i>Clupea sapidissima</i>).....	31.33	6.266	3.6455	94.78
“ “ (light meat).....	30.38	6.076	3.9352	90.09
“ “ (dark meat).....	32.63	6.526	3.5332	97.25
Salmon (<i>Salmo salar</i>).....	31.06	6.212	3.7345	87.32
“ “.....	31.50	6.300	3.6335	92.29
Tautog (<i>Hiatula onitis</i>).....	20.60	4.120	3.5660	89.80
Porgy (<i>Sparus chrysops</i>).....	22.56	4.512	3.5215	88.13
Blue fish (<i>Pomatomus saltator</i>).....	19.84	3.968	3.5885	87.03
“ “.....	19.46	3.892	2.9717	88.69
Mackerel (<i>Scomber scombrus</i>).....	25.51	5.102	3.4895	73.44
Halibut (<i>Hippoglossus vulgaris</i>).....	20.28	4.056	3.4600	86.24
Flounder (<i>Paralichthys dentatus</i>).....	23.04	4.608	3.4525	85.51
Sea Bass (<i>Serranus atrarius</i>).....	21.17	4.234	3.3995	85.32
Pike (<i>Esox lucius</i>).....	19.63	3.926	3.3582	84.01
Haddock (<i>Gadus aeglefinus</i>).....	18.24	3.648	3.3382	82.99
Herring (<i>Clupea harengus</i>).....	24.49	4.898	3.3317	82.50
Striped Bass (<i>Morone saxatilis</i>).....	20.73	4.164	3.2770	82.34
Red Snapper (<i>Lutjanus Blackfordi</i>).....	22.09	4.418	3.3040	80.99
Trout, brook (<i>Salvelinus fontinalis</i>).....	19.58	3.916	3.1745	81.65
Sea Robin (<i>Prionotus palmipes</i>).....	21.87	4.374	3.1572	78.45
White Perch (<i>Morone Americanus</i>).....	19.69	3.938	2.9515	78.03
Fresh Cod (<i>Gadus callarias</i>).....	18.29	3.658	2.9292	72.94
Weak fish (<i>Cynoscion regale</i>).....	19.78	3.956	2.9180	72.39
Yellow fish (<i>Perca Americana</i>).....	18.12	3.624	2.9037	72.11
Eel (<i>Anguilla rostrata</i>).....	21.78	4.356	2.9062	71.76
Window Pane (<i>Bothus maculatus</i>).....	18.37	3.674	2.8927	71.82
Flat fish (<i>Pleuronectidae Americanus</i>).....	17.15	3.430	2.7065	71.49
Lobster (young).....	21.75	4.350	3.5532	66.89
“ (large female).....	21.29	4.258	3.1990	87.81
“ (large male).....	20.76	4.152	2.7960	79.06
Crab.....	23.57	4.714	2.7165	69.13
Frogs' legs.....	17.86	3.572	3.2535	67.13

cerned, there was no appreciable difference in the three samples. Bearing in mind, however, these possible variations, it is very evident from our results that the average digestibility of fish flesh is far below that of beef similarly cooked. In but two instances, in the case of shad and lake white, does the digestibility of fish flesh approach that of beef, although, from the average of our experiments, several are as easily digestible as mutton, lamb and chicken.

Pavy¹ states that fish with white flesh, such as the whiting, etc., are less stimulating and lighter to the stomach, or more easy of digestion, than fish with more or less red flesh, as the salmon. Our experiments confirm this statement so far as digestibility is concerned. Thus the average digestibility of the salmon and trout is considerably below the average of the more digestible white fish. The difference between the digestibility of the light and dark meat of the same fish is somewhat striking, as in the case of the shad, where the digestibility of the former was found to be 97.25, as compared with beef, while the dark flesh was 87.32. A similar difference, though very much smaller, is to be noticed between the light and dark meat of the chicken.

This difference in digestibility is in part due, without doubt, to the amount of fat present, for, as Pavy states, in the flesh of white fish there is but little fat, it being accumulated mainly in the liver of the animal, while in red fish there is more or less fatty matter incorporated with the muscular fibres. For a similar reason eels, mackerel and herring are, according to Pavy, less suited to a delicate stomach than some of the white fish, and our experiments show that in digestibility two of them stand below the more digestible white fish; mackerel, however, from our single experiment with the white portion of the flesh, showed a comparatively high digestibility. In all of our experiments, however, with white fish, we rejected the outer layer of dark flesh, except in the case of the shad. The varying differences in digestibility are not to be considered as due wholly to differences in the amount of fat in the flesh; thus the flesh of fresh cod contains but little fat, and yet it is one of the most indigestible of the white fish experimented with. This agrees with Pavy's² experience "that it is a more trying article of food to the stomach than is generally credited." Again Pavy³ makes the following statement, based on his experience in fish dietetics, "of all fish, the whiting may be regarded as the most delicate, tender and

¹ On food and dietetics, Amer. ed., 1874, p. 171.

² *Loc. cit.* p. 173.

³ *Loc. cit.* p. 172.

easy of digestion." "The haddock is somewhat closely allied, but is inferior in digestibility," while "the flounder is light and easy of digestion, but insipid." With all these statements our results agree perfectly, assuming the lake white of our experiments to be analogous to the English whiting.

Maly,¹ in speaking of the digestive processes in the living stomach, says that raw flesh is more slowly digested than cooked, probably for the reason that with dilute acids the coagulated albumin of cooked flesh is more easily converted into acid albumin. Likewise, that the flesh of young animals is more rapidly digested than that of older, while fat flesh is but slowly attacked, as the melted fat surrounds the muscle fibres. With reference to the first of these statements, Jessen² found, by experimenting with perfectly lean beef of known age, that he had only a small undigested residue in an artificial digestion of the raw beef, but with the same amount of partially boiled beef a much larger amount remained undigested, and when thoroughly boiled a still larger residue was found. Taking the amount of undigested residue as a measure of the digestibility, the proportion with the same sample of beef was as follows: raw beef 100, partially boiled 167, thoroughly boiled 317. The gastric juice employed by Jessen, however, could hardly be considered as made up of a dilute acid, containing, as it did, 2.5 and 5.0 per cent. of concentrated hydrochloric acid.

In our own experiments, with a gastric juice containing but 0.2 per cent. of pure hydrochloric acid, positive results were obtained as follows:

	<i>1st sample of Beef.</i>		<i>2d sample of Beef.</i>	
	Raw.	Cooked (steamed).	Raw.	Cooked (steamed).
Amount digested from				
20 grams,	4.0792	3.8610	4.3785	4.1607
Relative proportion,	100.0	94.65	100.0	95.04

The difference here, then, is not so great, though sufficiently pronounced to indicate plainly the influence of cooking.

A similar experiment with a sample of blue fish gave a like result:

	Raw.	Cooked (steamed).
Amount digested from 20 grams,	3.7617	3.5885
Relative proportion,	100.0	95.39

¹ Hermann's *Handbuch der Physiologie* 5, 111.

² *Zeitschrift für Biologie* 19, 123.

With the *raw beef*, however, digestion was so near complete that a second experiment was tried with a larger quantity, as follows:

	From 20 grams.	From 30 grams.
Amount digested (raw beef),	4.3785	5.7610
Relative proportion,	100.0	131.57

This would make the relative digestibility of cooked (steamed) and raw beef as 100.0: 142.38, a difference nearly as great as that found by Jessen between raw and partially boiled beef. It is plain, then, that the digestibility of *raw* beef is considerably greater than cooked.

Whether the relative digestibility of raw and cooked fish, given above, would be changed by increasing the amount of flesh added, we cannot say. It is a point of little importance, but from the following experiment with cooked fish it probably would make but little difference. This experiment with cooked *sea bass* was tried mainly to ascertain the quantity of flesh best adapted to 200 cc. of our standard gastric juice:

	From 20 grams.	From 30 grams.	From 40 grams.
Amount digested,	3.3995	3.2325	2.5200
Relative proportion,	100.0	95.08	74.12

In this case, increasing the amount of material plainly diminishes the digestive action.

With regard to the second statement of Maly's, above quoted, our experiments tend to show that, in some instances at least, the flesh of younger animals is less easily digestible than that of older animals of the same species. This is well illustrated in the greater digestibility of mutton as compared with lamb.

AN IMPROVEMENT IN THE APPARATUS USED FOR PRECIPITATING COPPER BY ELECTROLYSIS.

BY HERBERT C. FOOTE.

Those who have occasion to make many determinations of copper by the electrolytic method have undoubtedly experienced some difficulty in always obtaining a current of proper strength, and, when the battery is to be used for two or three consecutive days, of keeping it so without changing the battery fluids.

I have devised a simple piece of apparatus which has saved me much trouble in this line, and as it has worked with extreme satisfaction in my laboratory for the past year, I beg leave to suggest its trial, at least, by those who have many copper determinations to make.

The platinum dishes are arranged on a board as shown in section by Fig. 2. The current from the battery, which is kept in a room in the basement, is carried by insulated wires to the laboratory, and made to pass through a certain number of coils of fine insulated iron wire before it passes to the platinum dishes.

Fig. 1 shows the under side of the board with the resistance coils and connecting wires sunken into it, so that no wires are visible above the board save the ones connected to the platinum strips dipping into the dishes.

The current enters at *a* and passes to *c*, where it enters a switch from which it may be made to pass directly to a switch at *g*, or it may be made first to traverse either one of the coils *m*, *n*, on its way, by a simple movement of the switch handle above the board. From *g* it may be made to pass through *h* to the switch at *r*, or by connecting the switch with *i*, *k* or *l*, the current will first traverse one, two or all of the coils *o*, *p*, *q*, and when it reaches *r* it will have the required strength. The coils have the following lengths of fine iron wire respectively: *m*, $1\frac{1}{2}$ metres; *n* and *o*, 3 metres each; *p* and *q*, $4\frac{1}{2}$ metres each.

More coils may be added if it is desirable, but with the arrangement shown in the cut a resistance of $1\frac{1}{2}$ metres may be obtained, which may be increased, by additions of $1\frac{1}{2}$ metres each, up to 15 metres, by properly manipulating the switches *c* and *g*. For example, if the switch *c* be connected with *e*, and the switch *g* with *i*, the current will pass through $4\frac{1}{2}$ metres of the iron wire.

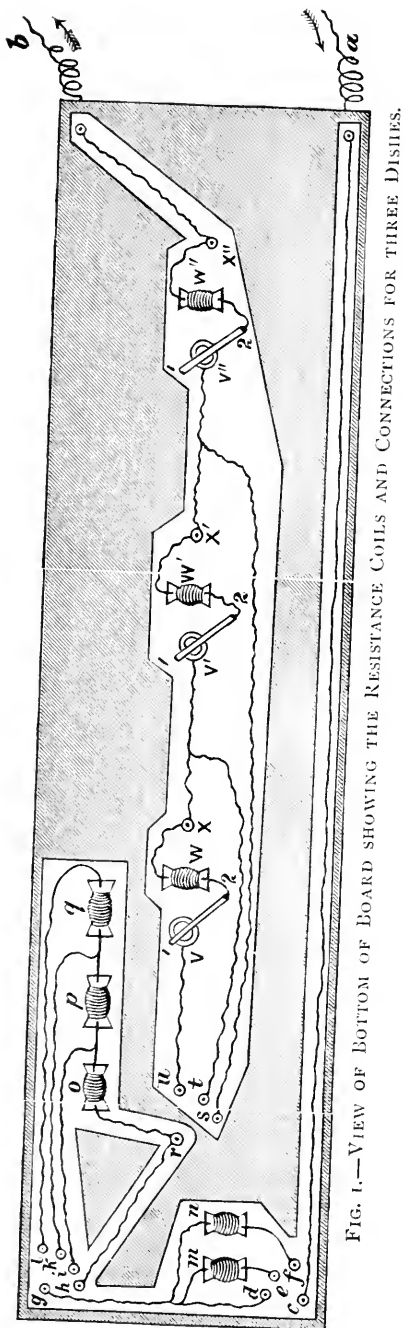


FIG. 1.—VIEW OF BOTTOM OF BOARD SHOWING THE RESISTANCE COILS AND CONNECTIONS FOR THREE DISHES.

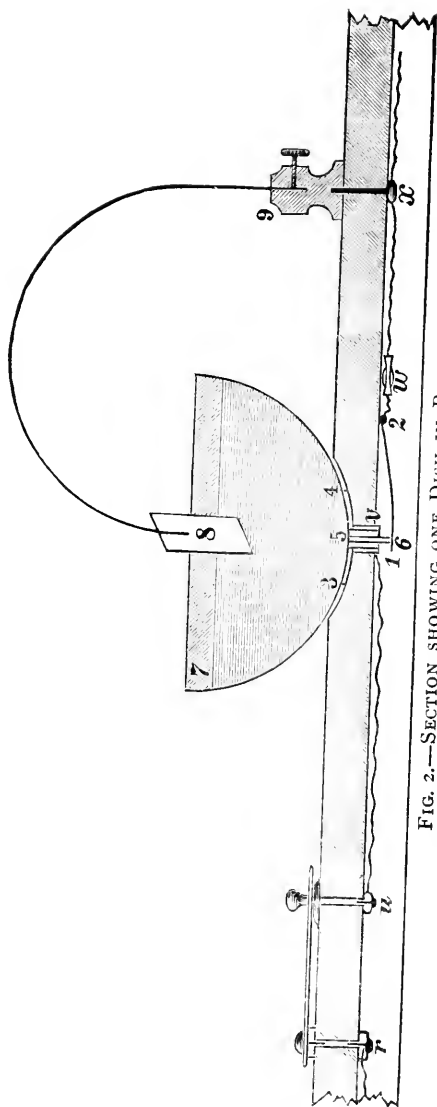


FIG. 2.—SECTION SHOWING ONE DISH IN POSITION.

The board shown in the cut is arranged for only three dishes, but it will be readily seen that any number might be added. As the battery grows weaker, or as dishes are removed or added to the circuit, the strength of the current is kept uniform by manipulating the switches. This might be made to work automatically.

The switch *r* with its connections *s*, *t* and *u* make it possible to use one, two or all of the dishes. If only one dish is to be used, the connection is made with *s*, and the current passes through the cylindrical copper connection *v''* (see also Fig. 2, *v*) to the platinum and finally through *x''* to *b*. If two dishes are to be used, the switch *r* is connected with *t*, and the current passes first to the dish over *v'*, thence through the platinum strip to *x'* and then to the second dish over *v''*. When all the dishes are to be used, connection must be made with *u*.

The method of automatically regulating the current in the case of removing a dish from the circuit is shown by Fig. 2. A coil of fine iron wire *w*, equal to the resistance of the solution in a dish, is placed under the board and near each dish. Through the centre of the piece of platinum 3, 4, upon which the precipitating dish rests when in connection with the current, is a small hole, which is continued down through the board and lined with a piece of copper pipe *v*, which is soldered to the platinum to make the connection. A short stick of wood 5, 6, passes through this pipe and is so arranged with a spring 1, 2, that when the resistance coil *w* is in the circuit, the stick protrudes slightly above the platinum foil. When, however, a dish is placed upon the board, it pushes down, by its weight, the stick 5, 6, removing the strip 1, 2, from contact with *v*, thus disconnecting the resistance coil and at the same time causing the current to pass from *v* through the solution and platinum strip to *x*. When a dish is removed, the current through 8, 9, is of course broken, and the spring 1, 2, comes in contact with *v* making the connection with the resistance coil, which, being equal to the resistance in the dish, keeps the current the same in the other dishes.

If two dishes are to be used, and the solution is only ready for one, the switch *r* is connected with *t*, and the dish which is ready is placed on the platinum above *v''*. The current will then pass from *t* to *v'*, and through the strip 1, 2, to the resistance coil *w'*, and thence through *x'* to *v''*, and finally through the liquid to *x''* and *b*. When ready to add the second dish to the circuit, it may be

done by simply placing the dish in its place over v' , when it will automatically disconnect the resistance coil w' , and the strength of the current will remain the same and sufficient for both dishes. Either one of the two dishes may now be removed at any time without altering the strength of the current, or in any way interfering with the work of the other dish in the circuit. The third dish may also be added at any time by simply changing the switch r from t to u and manipulating the switches c and g so as to increase the current sufficiently. In the same manner, any number of dishes may be used.

The strength of the current may be ascertained by passing it through acidulated water in an inverted tube graduated in cc. and noting the amount of mixed gases liberated in a minute; but I have found that a very little experience will enable one to tell when the current is suitable, by simply noting the rapidity with which the gas bubbles come off from the platinum strips in the liquid to be decomposed.

With the large number of determinations I have to make I find this arrangement of apparatus to be a great saving of time, and am sure it would be both neat and advantageous where only few analyses are to be made, and very desirable in the laboratory of a scientific school or college.

SYNTHETICAL RESEARCHES IN THE GLUCOSIDE GROUP.¹

III.

BY ARTHUR MICHAEL.

Identity of Natural and Synthetical Methylarbutin.

Several months after my note on synthetical methylarbutin appeared in the *Journal of the German Chemical Society*, H. Schiff obtained the natural compound in a pure state, and found in regard to melting point and water of crystallisation, that slight

¹ This Journal 1, 304; 5, 171.

differences exist between it and the synthetical product. This has led me to prepare the synthetical product in larger quantities than hitherto, and carefully compare its properties with those of the natural product. The methylarbutin used for this purpose was prepared from methylhydroquinol, obtained by the action of methyl iodide on hydroquinol, and was converted into the glucoside by the method already described in my previous paper. I also prepared methylarbutin from natural arbutin, according to the excellent method described by H. Schiff.¹

The melting point of the synthetical methylarbutin analysed by me was at 169° . I find that repeated crystallisation of the synthetical product from water gives a methylarbutin melting at 174.5° – 175.5° , and that natural arbutin, prepared according to Schiff's method, melted exactly at the same temperature.²

The following results were obtained in the analysis of synthetical methylarbutin melting at 174.5° – 175.5° :

0.2685 gram of substance, dried at 120° , gave 0.5346 gram of CO_2 and 0.1546 gram of H_2O .

	Theory for $\text{C}_6\text{H}_{11}\text{O}_5 - \text{O} - \text{C}_6\text{H}_4\text{OCH}_3$.	Found.
C	54.54	54.3
H	6.29	6.4

For ascertaining the water of crystallisation the substance was dried by exposure to the air, then at 100° , and finally at 120° .

0.4668 gram of air-dried substance lost 0.0286 gram of H_2O .

0.5285 gram of air-dried substance lost 0.03118 gram of H_2O .

	Theory for $\text{C}_{13}\text{H}_{18}\text{O}_7 + \text{H}_2\text{O}$.	Found.
H_2O	5.9	6.1 5.9

¹ *Annalen der Chemie* **221**, 366.

² The somewhat lower melting point given in my first paper is explained by the small quantity of synthetical methylarbutin at my disposal, which prevented repeated crystallisation. As an illustration of how an almost inappreciable amount of impurity may lower a melting point, I will state my recent experience with thiocarbanilide. Mr. G. M. Palmer and myself lately prepared this substance from phenylmustard oil and aniline, and found its melting point to be at 153° . The fact that the melting point hitherto given was at 144° , and that probably no organic substance has passed through the hands of a greater number of chemists, induced me to ascertain whether this carbanilide obtained from carbon disulphide and aniline is really the same compound. I found that eight crystallisations from absolute alcohol raised the melting point from 144° to 151° . It is evident that an impurity contained in carbon disulphide—I believe that none of the known methods of purification eliminate it completely—unites with aniline to form a compound having much the same solubility as thiocarbanilide. I shall endeavor to obtain the by-products of the carbon disulphide manufacture, and make them the subject of a chemical investigation.

This agrees with the result obtained by Schiff from natural methylarbutin.¹

It is also worthy of notice that synthetical methylarbutin, like the natural product, crystallises at times from very concentrated aqueous solutions in anhydrous crystals.

A further confirmation of the identity of the two products will be found in their behavior towards polarised light. The aqueous solutions of synthetical and natural arbutin turn the plane of polarisation to the left, and, apparently, to an equal degree.²

I believe the above-described experiments prove beyond a doubt that methylarbutin obtained by the action of acetochlorhydroses on potassium methylhydroquinol, and methylarbutin obtained according to Schiff's method from natural arbutin, are identical products.

That methylarbutin is contained in arbutin is rendered probable by these experiments, and placed almost beyond question by the recent research of Schiff,³ who treated the natural product with benzylchloride and then succeeded in separating methylarbutin by crystallisation. Habermann's⁴ paper may be considered as again showing the impossibility of separating arbutin from methylarbutin by crystallisation.⁵

¹ In the former analysis 3.5 per cent. of water was found. The substance analysed stood for upwards of a month in a room where the temperature frequently rose to 30° C., and there is no doubt that methylarbutin loses part of its water of crystallisation under these conditions.

² The instrument at my disposal was not sufficiently delicate to give the readings a scientific value. Tubes of equal length, containing equal quantities of the two products, could be interchanged in it without a noticeable change in the color of the disk.

³ *Annalen der Chemie* **221**, 366.

⁴ *Monatshefte für Chemie* **4**, 759.

⁵ J. Habermann has criticised my remarks on the constitution of arbutin in a very peculiar manner, and I take this opportunity of calling attention to it. I give the following as an illustration of Habermann's treatment of the work of other chemists: "He observed that methylarbutin does not melt at 175°, nor at 142°, as Schiff (*Berichte* **15**, 1842) has found, but at 169°; and also that the synthetical product is not colored by iron trichloride, whereas Schiff observed this property of all his crystallisations. It is not an easy matter to follow Michael in the statement: 'Die Eigenschaften (welche?) des Methylhydrochinons [Habermann has omitted glucoside, probably by mistake] scheinen mir entschieden für die Auffassung zu sprechen, dass das Arbutin ein Gemenge von Hydrochinon- und Methylhydrochinon-Glucosiden bildet.'"

This should be read with the following comment: Firstly, that synthetical methylarbutin agreed in its properties with natural arbutin, excepting in its behavior towards iron trichloride. Secondly, that I showed this property to be in accordance with our present knowledge of the behavior of iron trichloride towards aromatic phenols, and anticipated Schiff's proof, in a paper quoted by Habermann, who subsequently showed that iron trichloride gives no coloration with pure natural methylarbutin. Thirdly, that Schiff in the same paper showed the melting point of methylarbutin to be at 175°, and that his previous melting point—142°—was that of a mixture of arbutin and methylarbutin. Fourthly, that Schiff's paper appeared ten months later than my own, and it is, perhaps, excusable that I did not anticipate his correcting the melting point of methylarbutin from 169° to 175°. Fifthly, that several months before Habermann's paper appeared I expressed, in view of Schiff's results, the following determination: "I will prepare both products and carefully compare their properties" (*this Journal* **5**, 179).

Guaicol-glucoside.

The occurrence of methylarbutin in nature made it of interest to prepare glucosides synthetically which are isomeric with that compound. I have succeeded in preparing the glucoside of methylcatechol, while all experiments to obtain the corresponding resorcinol compound were without result.

Guaicol was prepared from the crude oil according to the directions given by Hlasiwetz,¹ and converted into the potassium derivative. Equivalent weights of the vacuum-dried salt and acetochlorhydrose were dissolved in absolute alcohol, the cold solutions mixed, and allowed to stand for three days. The deposition of salt began soon after mixing, and at the same time a perceptible odor of acetic ether became noticeable. The filtered solution was evaporated by exposure to the air, and after standing a long time partially solidified to form long needles. These were pressed between filter-paper, and crystallised four times from water.

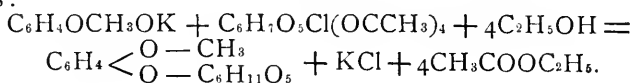
An analysis gave the following results:

0.2274 gram of substance, dried at 120°, gave 0.4569 gram of CO₂ and 0.1326 gram of H₂O.

Theory for C ₆ H ₁₁ O ₅ — O — C ₆ H ₄ OCH ₃ .		Found.
C	54.54	54.79
H	6.29	6.48

Guaicol-glucoside crystallises from water as fine, white needles, forming globular clusters. It is very soluble in hot water, moderately in cold. Sparingly soluble in cold alcohol, hot alcohol dissolves it more easily, and the glucoside separates from the solution as arborescent groups of needles. The crystals are sparingly soluble in hot benzene, and insoluble in ether. It melts at 156½°–157°, and has a very bitter taste. The glucoside is not decomposed by boiling with an aqueous solution of silver nitrate, nor by Fehling's solution. Heated with dilute caustic potash it decomposes into guaicol and dextrose only when heated for some hours. Dilute acids effect this decomposition almost immediately. The aqueous solution of the glucoside gives no coloration with iron trichloride.

The formation of guaicol-glucoside may be represented as follows:



¹ *Annalen der Chemie* **106**, 365.

Eugenol-glucoside.

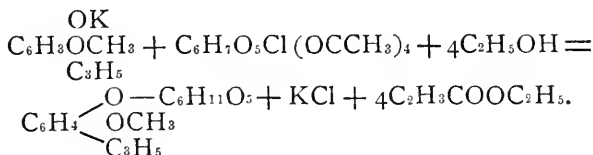
This compound is obtained by the action of acetochlorhydrose on potassium eugenol. The potassium derivative was prepared by dissolving potassium hydrate in a small amount of absolute alcohol, and adding the equivalent of eugenol to the solution. The crystalline salt, which separated from the mixture, was filtered, washed with absolute alcohol, pressed between bibulous paper, and dried *in vacuo*. A mixture of absolute alcoholic solutions of this salt and acetochlorhydrose, in equivalent proportions, was allowed to stand three days at the ordinary room-temperature, filtered from potassium chloride, and the filtrate evaporated by exposure to the air. After some days—from three to fourteen—the residue solidified to clusters of needles. These were pressed out and crystallised five times from water.

An analysis gave the following results:

0.2758 gram of substance, dried at 110°, gave 0.596 gram of CO₂ and 0.1717 gram of H₂O.

	Theory for C ₁₆ H ₂₂ O ₇ .	Found.
C	58.89	58.93
H	6.74	6.92

The formation of eugenol-glucoside is represented by the equation:



Eugenol-glucoside crystallises from water in white needles, melting at 132°. It is readily soluble in hot absolute alcohol, moderately in cold, and is insoluble in boiling ether and cold benzene. It dissolves in hot benzene and separates on cooling as a gelatinous mass, which has the same melting point as the crystalline substance. The aqueous solution reduces Fehling's solution on long boiling, but does not reduce an ammoniacal solution of silver nitrate; the addition of caustic potash to the solution, however, after heating a short time, causes the formation of metallic silver. Dilute acids decompose the glucoside readily into dextrose and eugenol.

Contribution from the Chemical Laboratory of Cornell University.

I.—THE BEHAVIOR OF IODIC ACID AS AN INDICATOR.

BY F. E. FURRY.

It is known that when free iodic and hydriodic acids are brought together in the proportion of one molecule of the former to five of the latter, a decomposition sets in which results in the liberation of all the iodine present in both acids. Consequently, if to a solution containing the neutral salts of these two acids in excess, some other acid which will displace them be added, the iodine set free will indicate the amount of the acid added.

This reaction¹ may be used for the purpose of an indicator in volumetric analysis, since the titration of the liberated iodine can be effected by sodium hyposulphite and starch, and thus the amount of acid brought in contact with the salts containing iodine be determined by one of the sharpest end-points known in volumetric analysis.

While employed, under the direction of Dr. Caldwell, in estimating small amounts of sulphuric acid by the application of this method as suggested by Kjeldahl,² the singular recurrence of the blue color after its discharge by hyposulphite came to notice, and was ascribed for some time to atmospheric carbonic acid, and to carbonic acid probably present in small quantities in the reagents and water used.

Kjeldahl's express statement³ to this effect has not been substantiated. While carbonic acid is known to bring about a slow liberation of iodine, experiments go to show that another cause is also operative.

With the supposition that the after-coloration was due to this acid alone, experiments were undertaken for the purpose of learning what other interferences, if any, are to be avoided, and how far the method is applicable.

A solution of sulphuric acid was accordingly made up, which contained 2.638 mgs. H_2SO_4 in every cc. A solution of sodium

¹ Mohr, *Titrimethode*, 315.

³ *Reper. der anal. Chemie*, III Jahr. 268.

² *Fres. Zeit.*, Bd. 22.

hyposulphite was also prepared by dissolving, approximately, 12.4 grams of the crystallised salt in a litre of water, and finally 8 grams potassium di-iodate (no neutral iodate being at hand) were dissolved in 200 cc. water and exactly neutralised with ammonia.

(1) *Delicacy of the end-point.* In order to ascertain the amount of acid necessary to produce a visible change in a neutral solution, in the absence of all interfering agents, 100 cc. freshly boiled distilled water, a small crystal of potassium iodide, 2 cc. of the iodate solution and a few drops of dilute sago paste were brought together in an Erlenmeyer flask. The mixture was perfectly colorless. As soon as the iodide was in solution, one drop ($= .08$ mg. H_2SO_4) was found to cause the liberation of sufficient iodine to change the liquid to a decided blue, and a like quantity of hyposulphite sufficed to discharge the color. It was not found difficult to pass back and forth in this way three times with .1 cc. standard acid. The delicacy of the end-point is seen to be much greater than that of many indicators in common use.¹

(2) *Influence of dilution.* 20 cc. acid ($= 52.76$ mgs. H_2SO_4) were brought into varying amounts of water, and a small crystal of iodide and 2 cc. iodate added. The titration with hyposulphite was nearly completed before the addition of starch; in this way the end-point can be approached to within 2 cc. without hesitation, and the flocks of iodised starch which are sometimes formed in the presence of a large excess of iodine, and which are as good as inaccessible to hyposulphite, are entirely avoided.

Experiment.	Cc. Water added.	Cc. Hyposulphite, immediately.	Additional cc. Hypo. in 15 min.
(a)
(b)	50	21.30	.05
(c)	100	21.21	.12
(d)	150	21.20	.15
(e)	400	20.60	.30
(f)	400	20.85	.15

In (a) the reading was not possible on account of the intervention of a brick-red color between the blue and colorless states, due, no doubt, to the presence of excess of iodide. If a true end-point could have been found, it is doubtful if it would have been of any value, on account of the fact that iodine vapors were distinctly

¹ Thompson, Chem. News **17**, 124.

seen above the solution. In (b) the red coloration was not present, but iodine vapor and odor could be faintly recognised after titration; no odor was recognised in the others. In (f) 8 cc. of iodate were used instead of 2 cc. as in the other cases.

The fact that dilution produces a difference is not mentioned by Mohr, and is directly denied by Kjeldahl; from the above and numerous others experiments, however, it seems incontestably proved that, for a given time, the liberation is less as the solution is more dilute. The water used in (e) and (f) was thoroughly boiled in a silver dish, and was so free from carbonic acid that a like portion containing iodide, 8 cc. iodate and starch showed no liberation of iodine whatever in 15 minutes, although freely exposed to the air in a beaker.

As a small amount of an alkaline carbonate present in the water would produce this difference, and as the water had been prepared by distillation from water rich in carbonates with the use of glass, an experiment was conducted in order to prevent the possibility of this error. 700 cc. distilled water were placed in a porcelain evaporator, 2 cc. of the standard acid added, and brought to brisk ebullition over a gas flame, where it was kept until the volume was reduced to 400 cc. After cooling as rapidly as possible by floating the dish in running water, the remainder of the 20 cc. acid was run in. Upon addition of iodide and 2 cc. iodate, a liberation immediately took place, requiring 20.53 hyposulphite for titration. In 15 minutes .3 cc. more was required.

Another evidence that the amount of dilution influences the action, is the fact that if the solution be diluted largely immediately after the main liberation has taken place, and then titrated, the after-liberation for a given time is less than if no extra water had been added.

The phenomenon of after-coloration is therefore ascribed almost wholly to the action of a residual quantity of the sulphuric acid, and only in a slight degree to atmospheric carbonic acid.

(3) *Behavior of the indicator with different acids.* From various phenomena noticed during the course of the work, it seemed advisable to try the action of acids other than sulphuric. Hydrochloric and nitric acids which had been standardised by titration against soda, using litmus as indicator, behaved precisely like sulphuric acid and can be substituted for it. Salicylic and picric acids are equally prompt and decisive, the after-coloration in both cases being very slight.

In the following table, a few of the other acids examined are given, with the amounts in mgs. of acid acting immediately, and after various periods of time counting from the addition of iodate and iodide. The acetic acid was standardised by soda with litmus. All the others were weighed out and an aliquot part of their definite volume solutions taken. After each titration, which occupied about fifteen seconds, the flask was corked. In every case 100 cc. water were used and 21.21 cc. hyposulphite taken as equal to 51.76 mgs. H_2SO_4 .

Acid used.	Wt. of acid used in mgs.	Milligrams of acid found from iodine liberated.				
		Immediately.	After 5 min.	After 15 min.	After 30 min.	After 1 hour.
Boracic.....	206.0	none.	none.	none.	none.	none.
Boracic	2060.0	"	1.6	...	3.2	4.1
Tartaric.....	79.87	64.48	69.79	72.44	73.58	74.92
Citric	74.55	31.84	40.70	42.37	44.24	46.72
Oxalic.....	67.91	56.08	58.95	60.24	61.19	61.67
Acetic	64.62	24.27	33.67	36.70	40.34	43.98
Benzoic.....	110.0	60.61	73.98	78.98	82.87	85.92

Dilution of the solution was found to affect oxalic less than acetic and citric acids, but neither these nor tartaric, benzoic or (much less) boracic, could be made to liberate their full equivalents of iodine or give rates indicating such a final result.

After fifteen hours, the oxalic acid solution, which had been corked immediately after the titration, shown last in the table, showed a liberation of only 1.88 mgs. more. Under like conditions the tartaric acid solution showed 3.22 mgs. more, after forty hours.

(4) *Behavior in the presence of neutral salts.* Four grams of each of the following salts were dissolved in 100 cc. water and the iodide, iodate and 52.76 mgs. H_2SO_4 added.

Salt used,	Cc. Hypsulphite.
Ammonium chloride,	21.22
Ammonium sulphate,	21.20
Ammonium nitrate,	21.20
Sodium acetate,	none.
Ammonium oxalate,5

When varying amounts of sodium acetate were used, varying amounts of iodine were liberated :

Grms. Sod. Acet.	Cc. Hypos. used immediately.					
1.0	none.
0.52
0.4	1.2
0.3	2.2
0.2	7.5
0.1	14.5
0.05	18.5

All citrates, tartrates, oxalates and acetates tried, offered a like obstacle to the liberation, while the chlorides, sulphates and nitrates of ammonium, sodium and potassium, did not, unless present in large quantities. When the liberation took place in saturated or almost saturated solutions of the latter salts there was sometimes a slight retarding and blurring of the end-point, and sometimes the blue was followed by red. In practice, therefore, reasonable amounts of the neutral ammonium, sodium or potassium salts of the three strong acids can be present, but even small amounts of salts of the organic acids render the method uncertain. Borates also interfere. The interference of their neutral salts is a partial explanation of the incomplete action of the organic acids.

In conclusion, the method is certainly worthy of more general use, and must meet with favor whenever given a fair trial. An interesting test of the delicacy of other indicators can be made by neutralising a solution by them, and then adding some iodine, iodate and starch. An acidity not shown by methyl orange gives, in this way, an intense blue.

The slight dependence of the liberation on the amount of dilution and length of time cannot be looked upon as seriously impairing the method, as these interferences can be easily controlled by having the reaction always take place in similar volumes of solution, and completing the titration directly. When 100 cc. water are present, the end-point is made more satisfactory by preceding the titration with 50 cc. water, which, as already said, so dilutes the residual acid as to postpone its action still farther, but has no influence whatever on the iodine already free.

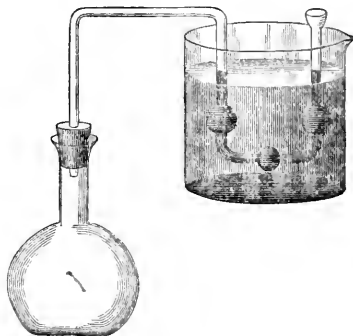
A NEW METHOD FOR THE DETECTION OF IODINE,
BROMINE AND CHLORINE.

BY EDWARD HART.

If nitrates, chlorates, bromates or iodates are present, it is necessary to fuse the substance with a little sodium carbonate and charcoal to reduce them.

If the haloids are united with silver it is best to fuse with sodium carbonate and extract with water, although with iodine and bromine this is not absolutely necessary. (See exp. No. 8, below.)

The substance is placed in the flask, shown in the figure, with some water and a few drops of a solution of ferric sulphate. Into the bulbs is poured a few drops of dilute starch paste. The bulbs are kept cold by immersing in water in a beaker. The contents of the flask are then boiled, and if iodine is present the starch is colored blue. This test is extremely delicate. If iodine is found, the cork with the bulb tube is removed and the solution boiled until, on testing again in the same way, no more iodine is found. If much iodine is present it is necessary to add more ferric sulphate solution. The bulb tube is now cleaned, charged with a few drops of water and a drop or two of chloroform, and a very small crystal of potassium permanganate is added to the solution in the flask.



The contents of the flask are boiled again and if bromine is present the chloroform becomes red. The tube is now removed and more potassium permanganate and ferric sulphate solution added, little by little, boiling after each addition until the bromine has all been driven off. A few drops of alcohol are added to the contents of the flask to decolorise any excess of permanganate, and after filtration, chlorine is tested for in the filtrate with silver nitrate.

The flask shown in the figure holds about 60 cc. and the bulbs are blown on a piece of common tubing about 5 mm. outside diameter.

Mixtures were given to three students, in qualitative analysis, neither of whom had used the test, with the following result:

No.	Contains.				Reported.	
A	{	1	2 grams NaCl	.001 gram KI	.005 gram K Br	I, Br, Cl
		2	2 grams NaCl	.001 gram KI	.002 gram K Br	I, Br, Cl
		3	2 grams NaCl	.001 gram KI	.001 gram K Br	I, Br, Cl
		4	2 grams NaCl	.001 gram KI	I, no Br, Cl
		8	2 grams NaCl	.001 gram AgI	.001 gram Ag Br	I, Br, Cl
B	{	5	2 grams NaCl002 gram K Br	No I, Br, Cl
		6	2 grams NaCl	.001 gram PbI ₂	I, no Br, Cl
		9	1 gram NaCl	.001 gram KI	2 grams K Br	Trace I, Br, Cl
C	{	10	.001 gram NaCl	.001 gram KI	.001 gram K Br	I, Br, Cl
		11	.001 gram NaCl	.001 gram KI	2 grams K Br	Trace I, Br, Cl
		12001 gram KI	2 grams K Br	Trace I, Br, no Cl

As in testing No. 3, only about one-tenth of the amount of substance given out was used for testing, it is evident that an ordinary student can by this method detect the bromine in .0001 gram potassium bromide, and a very much smaller amount of potassium iodide can easily be found. It is also evident from 9, 11 and 12 that the presence of a large amount of bromine decreases the delicacy of the test for iodine.

The solution of ferric sulphate is made as follows: Copperas is dissolved in water, oxidised with nitric acid, the solution precipitated with ammonia and the precipitate washed by decantation, and finally brought on a filter. 50 cc. of dilute sulphuric acid (1 acid to 1 water) is saturated with the still moist precipitate, and to the solution 50 cc. of the same dilute sulphuric acid is added.

LAFAYETTE COLLEGE, Nov. 1884.

A SIMPLE APPARATUS WHICH ENABLES STUDENTS TO DETERMINE THE EQUIVALENTS OF CERTAIN ELEMENTS.

BY H. N. MORSE AND E. H. KEISER.

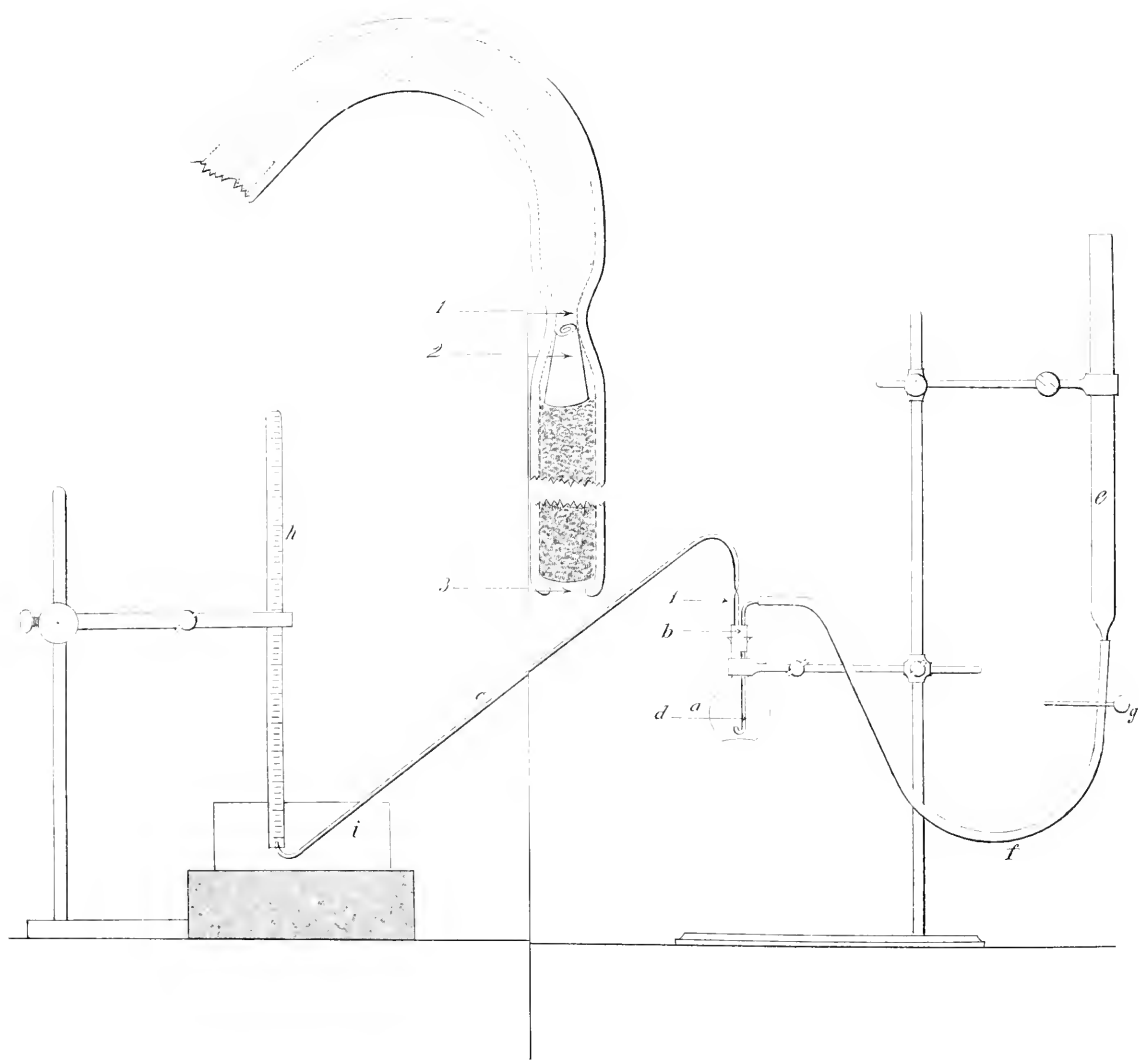
The design of the first year's course of laboratory work for undergraduates in this university is to teach the important facts of general chemistry. During that time analysis is taught only incidentally. The course begins with a series of exercises in manipu-

lation and in the calculations incidental to quantitative chemical work, each exercise being preceded by a lecture, in which the subject matter is explained or illustrated, and the student warned against the errors which he is likely to make. This division of the course includes such exercises as: the manipulation of glass; the setting up of apparatus; the various operations connected with the solution and precipitation of substances; the collection and washing of precipitates; the use of the blow-pipe; recrystallisation; sublimation; distillation; the use of the balance; the measurement of liquids and gases; and the correction of gas volumes to standard conditions of temperature and pressure.

The student, having thus acquired some understanding of laboratory processes and some skill in manipulation, begins to experiment upon the elements and their compounds—first of all upon hydrogen. Throughout the remainder of the course much attention is given to enabling the student to demonstrate for himself the quantitative relations of the various substances with which he works. Great care is taken, however, to keep out of his hands such apparatus and such methods as give results which approximate only roughly to the true ones; because results of this character are believed to be not only destitute of educational value, but positively demoralising to the student. The determination of the equivalence of the elements by the students is naturally regarded as very important, because that is the fact on which most of our chemical reasoning is based. In connection with his first piece of experimental work the student determines the equivalence of some of the metals in terms of hydrogen. For this purpose the simple apparatus here described is employed. The results obtained with it have been so generally and so thoroughly satisfactory, that we venture to publish a description of it for the benefit of those who may be following a similar course of laboratory instruction.

The apparatus consists of:

- a.* A flask having a capacity of 40 or 50 cc.
- b.* A rubber stopper having two holes. The stopper should fit the neck at all points so tightly that no gas can lodge between it and the glass.
- c.* A small glass delivery tube of the form indicated, which ends at the lower surface of the stopper. The upright portion of this tube is somewhat contracted at 1, as shown in the enlarged figure. A rather tightly fitting conical roll of platinum foil is placed at 2.





The remainder of the tube between the platinum roll and 3 is filled with glass wool. The opening at 3 is narrowed down, after the glass wool has been introduced, by allowing the glass to soften in the flame.

d. A second glass tube which nearly touches the bottom of the flask and turns up at the end. The opening of this tube is also contracted.

e. A glass tube holding about 100 cc., which serves as a reservoir.

f. A small rubber tube with thick walls, which connects *e* with *d*.

g. A Mohr's pinch-cock, which serves to open or close *f*.

h. A calibrated, 100 cc., gas measuring tube graduated to $\frac{1}{10}$ cc.

i. A glass dish.

The apparatus can be employed to determine the equivalents of all those metals which liberate hydrogen in equivalent quantities when treated with acids or caustic alkalies; provided, of course, such metals can be obtained in a sufficiently pure condition. The metals which we usually employ as examples are zinc and aluminium.

The experiment is conducted in the following manner :

e is filled with distilled water; a piece of zinc weighing from 0.150 to 0.200 gram is placed in the flask; the pinch-cock *g* is then opened and the whole apparatus allowed to fill with water. The apparatus is now examined in order to ascertain if gas bubbles are lodged under the stopper *b*, or in the glass wool. If so, they can usually be dislodged without difficulty. If they persist, a few moments' boiling of the water in the flask will effect their complete removal. Having thus effected the complete removal of the air from the apparatus, the eudiometer is placed over the outlet of the delivery tube, and the greater portion of the water remaining in *e* allowed to flow through the apparatus. Sulphuric acid of the concentration ordinarily employed in the laboratory (1 of H_2SO_4 to 4 of H_2O) is poured into the reservoir *e* until it is nearly full. The pinch cock *g* is then opened and the water which fills the apparatus is displaced by sulphuric acid. The action of the acid upon the metal may be facilitated by heat or by adding some platinum scraps. When the action is over, the contents of the flask are swept through the delivery tube by again opening the pinch-cock *g*. Finally, the eudiometer is transferred to a cylinder of water, the volume of the gas read and corrected in the usual manner. If hydrochloric instead of sulphuric acid has been used, which would be the case

when the metal employed is aluminium, a little caustic soda should be added to the water in the cylinder to which the eudiometer is transferred.

We give below a number of examples of the results obtained by our students during the present academic year.

A. obtained from

.1045 gram Zn, .003223 gram H_2 , or the equivalent 32.42.

.1070 gram Zn, .003306 gram H_2 , or the equivalent 32.37.

B. obtained from

.07475 gram Zn, .00229 gram H_2 , or the equivalent 32.53.

.0729 gram Zn, .00224 gram H_2 , or the equivalent 32.56.

C. obtained from

.1098 gram Zn, .003375 gram H_2 , or the equivalent 32.54.

.1400 gram Zn, .004307 gram H_2 , or the equivalent 32.50.

D. obtained from

.1180 gram Zn, .00364 gram H_2 , or the equivalent 32.40.

.0925 gram Zn, .00283 gram H_2 , or the equivalent 32.62.

E. obtained from

.1025 gram Zn, .003167 gram H_2 , or the equivalent 32.36.

.0610 gram Zn, .0018852 gram H_2 , or the equivalent 32.36.

To test the working of the apparatus, three experiments were made by ourselves:

We obtained from

.1959 gram Zn, .00602 gram H_2 , or the equivalent 32.55.

.1646 gram Zn, .00507 gram H_2 , or the equivalent 32.48.

.1436 gram Zn, .004419 gram H_2 , or the equivalent 32.49.

The following list contains all of the results which have been obtained with zinc by the members of our class of first year students during the present year:

32.34	32.44	32.36	33.20	32.30
32.63	32.50	32.55	32.30	32.40
32.66	32.54	32.38	32.80	32.57
32.60	32.53	32.45	32.70	32.42
32.80	32.37	32.46	32.40	32.41
32.30	32.56	32.32	32.60	32.40
32.50	32.87	32.62	32.20	32.20
32.84	32.36	32.36	32.50	32.30
32.69	32.63	32.60	32.20	32.40
32.53	32.37	32.56	32.62	32.37
32.42				

The results obtained with aluminium are not less satisfactory, but enough data have already been given to demonstrate that the apparatus answers very well the purpose for which it was devised.

We use the same apparatus, with some modifications which will be described hereafter, for the determination of the commercial value of zinc dust.

JOHNS HOPKINS UNIVERSITY, Nov. 1884.

REVIEWS AND REPORTS.

REPORT ON PROGRESS IN ANALYTICAL CHEMISTRY.

Halogens.

Determination of Halogens in the Side-Chains of Aromatic Compounds (K. E. Schulze).¹—The method is based on the fact that, when halogen derivatives of aromatic compounds are boiled with an alcoholic solution of silver nitrate, all of the chlorine, bromine or iodine contained in the so called side-chains is precipitated, while that contained in the groups peculiar to aromatic compounds is undisturbed.

The substance is weighed into a small flask, and an excess of a hot saturated alcoholic solution of silver nitrate is added. The flask is attached to an inverted condenser, the tube of the condenser being introduced far enough to prevent the vapors from coming in contact with the stopper. The contents of the flask are boiled for five minutes, and filtered while hot. Instead of collecting on filter paper, the author uses a platinum crucible with a perforated bottom, upon which there is a layer of finely divided asbestos. The precipitate is washed successively with alcohol, with water acidulated with nitric acid, and again with alcohol. The method is much more expeditious than that of Carius; and, in all the cases in which it has thus far been tried, it gave satisfactory results.

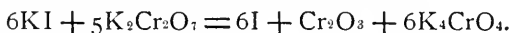
On the Determination of Chlorine in Urine (Michailow).²—The determination of chlorine by Mohr's method is not applicable to urine, because silver nitrate is decomposed by uric acid and the pigments of the urine. Volhard's method may be used,

¹ Berichte d. deutsch. chem. Gesell. 17, 1675.

² Journ. d. russ. phys.-chem. Gesell. 1884, 177.

but it is less expeditious. Michailow finds, however, that the former method can be employed, if the urine is previously filtered through animal charcoal. By this means the uric acid and the coloring matters are removed, while the sodium chloride passes through without absorption.

Separation of Iodine and Chlorine by a dry method (J. Krutwig).¹—When a dry mixture of potassium iodide and potassium bichromate is heated the iodine is liberated, and there is formed chromium sesquioxide and potassium chromate,



If the mixture is weighed before heating, and the heating continued until no more iodine vapors escape, the loss of weight denotes the quantity of iodine which was present. Or, the fused mass may be treated with water. Everything but the chromium sesquioxide will be dissolved, and from its weight, the quantity of iodine which was present can be calculated. Sodium chloride, on the other hand, is not changed when fused with potassium bichromate.

On the action of Bromine and Iodine upon Silver Bromide, Chloride and Iodide (P. Julius).²—By passing a mixture of air and bromine vapor over heated silver iodide, the author finds that the iodine is completely replaced by the bromine, and pure silver bromide is obtained. In the same way, by passing bromine vapor over heated silver chloride, the chlorine is replaced by bromine. Even iodine vapors, when passed for a sufficient length of time over heated silver chloride, or silver bromide, decompose them with the formation of silver iodide, free chlorine, and bromine respectively. The conclusion is that either halogen, if used in excess, is capable of replacing the others when united with silver.

Estimation of Chlorine, Bromine and Iodine in the presence of one another (F. Maxwell-Lyte).³—The haloids having been precipitated together with silver, the precipitate is to be collected, dried, and weighed. It is then dissolved in about thirty or forty times its weight of water by the addition of the least possible quantity of potassium cyanide. A quantity of pure potassium bromide is now added, which need not be above the weight of the precipitate. The cyanide is then decomposed by the addition of an excess of dilute sulphuric acid. The precipitate, in which any silver chloride has become by this means converted into silver bromide, is now collected on a filter, dried and weighed. It is once more dissolved by the least possible quantity of potassium cyanide and the same quantity of water, and to this is then added one and a quarter times the original weight of the precipitate of potassium iodide. The cyanide is now again decomposed by dilute sulphuric acid, and the precipitate once more collected on a filter, dried and weighed. In this last precipitate all the

¹ Berichte d. deutsch. chem. Gesell. **17**, 341.

² Zeit. f. anal. Chem. **22**, 523.

³ Chemical News 1884, 3.

silver is converted into iodide, excepting such as was iodide already. In the second experiment all became bromide, excepting such as was bromide or iodide already. From the weights thus obtained from the first, second and third weighings, the chlorine, bromine and iodine may easily be calculated."

Determination of Iodine in a mixture of Iodides, Bromides and Chlorides (A. Cavazzi)¹.—From a mixture of chlorides and iodides the iodine can be isolated by a boiling solution of neutral ferric chloride; but if bromides are also present, the bromine is liberated as well. To remove iodine from a mixture of chlorides, bromides and iodides, the author uses ferric sulphate which has been previously heated to redness. As the calcined salt dissolves with difficulty in water, a little ferrous sulphate is added, which increases the solubility and renders the solution permanent. Two grams of ferric sulphate in the presence of .1 to .2 gram of ferrous sulphate dissolve readily in 25 cubic centimeters of water. The mixture of chloride, bromide and iodide is then boiled with this solution. The iodine separates out and is absorbed in potassium hydroxide, the iodate of potassium is then reduced to iodide with hydrogen, which is evolved in the alkaline solution by means of aluminium. The iodine in the potassium iodide is determined in the usual way, with silver nitrate.

On the use of neutral Potassium Chromate in preparing standard iodine solutions (Léon Crismer)².—The author obviates the difficulties connected with the preparation of standard iodine solutions by making a standard solution of neutral potassium chromate (1.9396 grams to the litre). When this solution is added to a solution of potassium iodide previously acidified with sulphuric acid, the following reaction takes place:



that is, one molecule of potassium chromate liberates three atoms of iodine. A cubic centimeter of a centinormal solution of potassium chromate, therefore, corresponds to 0.0037957 gram of iodine. To make a standard iodine solution it is only necessary to add 100 cc. of centinormal potassium chromate to 20 cc. of a 20 per cent. solution of potassium iodide in a graduated flask, and after adding 20 cc. of dilute sulphuric acid (1:4), to fill to the mark with distilled water. If the flask holds 300 cc. the solution will be exactly a centinormal iodine solution. The author finds centinormal solutions better adapted for titration with sodium hyposulphite than decinormal, because the end of the reaction can be determined with greater accuracy in the dilute solution.

Water.

An absorbing Apparatus for Elementary Analysis (C. Winkler)³.—In endeavoring to dry large volumes of gases by passing

¹ Chemical News **49**, 14.

² Berichte d. deutsch. chem. Gesell. **17**, 642.

³ Zeit. f. anal. Chem., 1882, 545.

them through U tubes filled with calcium chloride, the author found that not only aqueous vapor, but also appreciable quantities of carbon dioxide were removed from the gases. A current of dry carbon dioxide had previously been passed through the U tubes to neutralise the calcium oxide which is always present in commercial calcium chloride. Further examination showed that it is impossible to completely neutralise all the calcium oxide contained in the granular calcium chloride by passing dry carbon dioxide through the tubes; nor could the object be attained by the use of gaseous hydrochloric acid; for, in both cases, it is only on the exterior of granules that the calcium oxide is neutralised, while the interior remains unacted upon. Now when moist gases are passed through drying tubes prepared in this way, the exterior of the granules is soon dissolved by the water, and the calcium oxide is exposed, which then absorbs carbon dioxide. Even repeated heating of the calcium chloride with ammonium chloride was not sufficient to completely convert the oxide into chloride. It is, therefore, recommended that sulphuric acid be employed instead of calcium chloride for absorbing water in elementary analysis. Instead of U tubes containing pumice stone saturated with concentrated sulphuric acid, Winkler uses his "spiral absorption apparatus." This consists of a glass tube (6 mm. diameter), bent in the form of an ascending spiral, and so arranged that the bubbles of gas enter at the bottom and slowly pass up around through the successive coils of the spiral. The gas bubbles are thus brought, at every stage of the ascent, in contact with fresh portions of the absorbing liquid.

The author also adapts his method to the analysis of organic compounds containing sulphur. A known quantity of chromic acid is added to the sulphuric acid; the sulphur dioxide formed during the combustion is thus retained, and its quantity can be readily determined by titrating the excess of chromic acid.

Note on Prof. Winkler's Communication concerning an Absorption Apparatus for Elementary Analyses (W. Mathesius).¹—The author endeavored to substitute sulphuric acid for calcium chloride, as a drying agent in elementary analyses, as had been suggested by Winkler, but found that the caustic potash bulbs constantly increased in weight when air free from carbon dioxide was drawn through the apparatus. He then tried sulphuric acid of varying concentration, and found that there was still an increase in weight of the potash bulbs, even when the specific gravity of the acid had been reduced to 1.71. Experiments with calcium chloride showed conclusively that appreciable quantities of carbon dioxide are retained by it; thus confirming Winkler's statement. Mathesius, therefore, rejects both calcium chloride and sulphuric acid, and uses phosphoric anhydride

¹ Zeitschrift für anal. Chemie 23, 345.

instead. The substance gave satisfactory results. There was no increase in the weight of the soda lime tube on drawing air free from carbon dioxide through the apparatus. In cases where the water formed by combustion is to be determined, it is necessary to pass the oxygen through a tube containing phosphoric anhydride before it enters the combustion tube.

On Liquid Paraffin. Its application as a reagent for the detection of Water in Alcohol, Chloroform and Ether (Léon Crismer).¹

—Liquid paraffin is an oily substance, consisting of a mixture of hydrocarbons of the marsh gas series, which boils between 125–240° under a pressure of 6 mm. It mixes with chloroform and ether in all proportions, forming a clear liquid, provided the chloroform and ether have previously been treated with metallic sodium to remove all water. The addition of a very small quantity of water or aqueous alcohol is sufficient to produce a turbidity in these solutions. This fact may be employed as a means of detecting water in chloroform or ether. In the same way, absolute alcohol dissolves a certain amount of liquid paraffin, forming a perfectly clear solution. A trace of water is, however, sufficient to produce a distinct turbidity.

The author also used liquid paraffin for the preparation of hydrobromic and hydriodic acids. A weighed quantity of phosphorus in the form of sticks is introduced into a flask and covered with liquid paraffin. A quantity of bromine necessary for the formation of phosphorus tribromide is then gradually added; the flask being kept cool by immersing it in water. A regular evolution of hydrobromic acid may then be obtained by allowing water to enter the flask drop by drop. Hydriodic acid is prepared in a similar way.

Hydrogen Dioxide. A new reaction for the detection of Hydrogen dioxide (M. Traube).²—Schönbein's reaction for the detection of hydrogen dioxide, by means of potassium iodide, starch and iron sulphate, requires a neutral solution. In the presence of free acid the reaction is very much less sensitive; and in very strong acid solution it is impossible to detect minute quantities of the dioxide. The author has found that the reaction loses none of its sensitiveness in strongly acid solutions, if a small quantity of copper sulphate is present. If to 6–8 cc. of a solution containing potassium iodide, starch, and minute traces of hydrogen dioxide, from 1 to 4 drops of a 2 per cent. solution of copper sulphate, and a little of a $\frac{1}{2}$ per cent. solution of ferrous sulphate are added, a blue color will be produced in very few seconds.

¹ Berichte d. deutsch. chem. Gesell. **17**, 649.

² *Ibid.* **17**, 1062.

ON THE MAGNETIC ROTARY POLARISATION OF COMPOUNDS IN RELATION TO THEIR CHEMICAL CONSTITUTION.

Since the time of Faraday's discovery of magnetic rotary polarisation, the influence of magnetism on the power of chemical substances to rotate the plane of polarisation has frequently been the subject of investigation, but no definite relationship between chemical composition and this power had been discovered up to within a short time. Recently, however, the distinguished English chemist, W. H. PERKIN,¹ has succeeded in showing by an elaborate investigation that a definite relationship between the chemical constitution of substances and their magnetic rotary powers does exist. He first pointed out "that no relationship of this kind was likely to be found by the usual method of calculating the results of the observations—which consists in comparing the magnetic rotary effect of unit lengths of the fluid bodies—but that if unit lengths of vapor could be examined, some useful information might be obtained, because these lengths would be occupied by equal numbers of molecules. But as an examination of this kind would present very serious difficulties, it was shown how the same end might be attained by referring the results of the observations obtained by the examination of unit lengths of fluids to the lengths of columns of liquid which would be formed by the condensation of unit lengths of their vapors; in other words, to lengths related to each other in proportion to their molecular weights, making the necessary correction for difference of densities. This can be effected by the simple formula

$$\frac{r \times Mw}{d},$$

r being the rotation observed, Mw the molecular weight, and d the relative density. This calculation having been made, both for the substance under examination, and also for the standard with which it is compared, it is only necessary to divide the result obtained from the former by that of the latter, and the product will be the 'molecular coefficient of magnetic rotation,' or, more briefly, the 'molecular rotary power.'"

All the substances examined, about 140 in number, were purified with the greatest care. The method of work was in brief as follows: Monochromatic light produced by burning hydrogen charged with the vapor of metallic sodium was first passed through a solution of potassium bichromate, then through the polariser of the polarising apparatus, through one of the poles of a strong electro-magnet, and then through the substance under observation, which was contained in a glass tube between the poles of the magnet. After emerging from the substance, the light passed through the other pole of the magnet, and finally through the

¹Journal of the Chemical Society 1884, 421; see also 1882, 330.

analyser. The strength of the electric current passing through the coil of the electro-magnet was measured by means of a tangent galvanometer of peculiar construction; and in each series of observations on the same substance the strength was kept constant with the aid of a resistance coil. Difficulty was met with in trying to use the relative densities already published. Hence it was found necessary to take the density of all the substances before they were examined, as it is an important factor in the calculation of the molecular rotation.

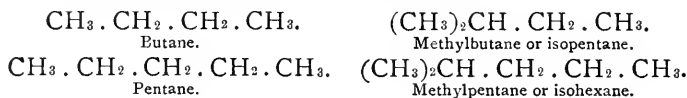
The effect of an addition of CH_2 to a compound is to increase its molecular magnetic rotation by 1.023, a figure deduced from a very large number of observations. "Having obtained this result, it is found possible to calculate the molecular rotation of any member of a homologous series if but one member be well examined, all that is necessary being to add or subtract this number as many times as the difference of composition may require. Taking α -nanthylic acid, $\text{C}_7\text{H}_{14}\text{O}_2$, as an example, if we take its molecular rotation and subtract from it 1.023×7 , we get a residue in excess of that which the product would give if it consisted of CH_2 only, thus:

$$\begin{array}{rcl} \text{Mol. rotation of } \alpha\text{-nanthylic acid,} & . & 7.552 \\ 1.023 \times 7, & . & 7.161 \\ \hline & & 0.391 \end{array}$$

"This residual number it is proposed to call the *series constant*, and designate by s . From this we may construct a formula for the normal acids of this series (commencing with propionic acid)— $\text{C}_n\text{H}_{2n}\text{O}_2 = 0.391 + n(1.023)$."

On comparing the figures calculated by means of this formula with those which are the results of actual measurements, close agreement is observed. The series constants differ for different classes of compounds. Thus for ethereal salts it is 0.337; for the paraffins it is 0.513; for the aldehydes, beginning with propyl aldehyde, it is 0.263, etc.

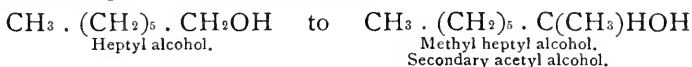
The series constants above given are those for the normal compounds. Isomeric series give different figures. The first effect studied is that produced by the displacement of hydrogen by methyl in normal homologous compounds. The isoparaffins, for example, "may be considered as normal paraffins in which an atom of hydrogen has been displaced by methyl in the CH_2 group already associated with methyl, thus:



"The influence of the introduction of methyl on the molecular rotation is very marked, as it increases the rotation to a con-

siderably greater extent than would result from the change in composition caused by the introduction of CH_2 ." In the same way a similar increase in the molecular rotary power is caused by the introduction of methyl in the place of hydrogen in alcohols, acids and aldehydes. In studying the acids it was found that formic and acetic acids conduct themselves differently from the other members. In regard to this the author observes: "From the numbers which have been obtained, and from a consideration of the subject, it appears that any body to be the first member of a homologous series must contain the CH_2 -group, because it is by the introduction of additional members of this group that we form these series. Thus propionic acid should be the first member of the homologous series of acids. Formic and acetic acids do not contain the CH_2 -group, and they are well known to possess properties which are not altogether comparable with those of the other fatty acids. The magnetic rotation of these bodies, as referred to above, indicates the same thing."

As further illustrations of the kinds of results obtained the following may be mentioned: The influence of the displacement of hydrogen in normal bodies so as to form secondary compounds, as for example in the change from—



seems to be about the same as when methyl is introduced in such a manner as to form iso-derivatives. When the hydrogen of an aldehyde is displaced by methyl so as to form ketones, the molecular rotation is increased in the same way as when normal aldehydes are converted into iso-aldehydes. The effect of the conversion of an acid into its ethyl salt is to reduce its magnetic rotation, while the displacement of the hydrogen of the hydroxyl of an acid by methyl produces a greater reduction of the magnetic rotation than does that of ethyl. The introduction of carboxyl causes a reduction in the magnetic rotation of alcohol radicals when associated with it, although the rotation of the group itself is evidently high. As regards the effect of hydroxyl the statement is made "that both in the series of the paraffins and the aldehydes, the introduction of hydroxyl in place of hydrogen increases the molecular rotation; but in the latter case the influence is somewhat smaller, due undoubtedly to the existence of carbonyl, CO , in the compound." On comparing the molecular rotation of a paraffin with that of the corresponding aldehyde and acid, it is "found that oxygen when displacing two hydrogens on the same carbon has nearly double the influence which it has when simultaneously combined with carbon and hydrogen." Unsaturated bodies show a larger molecular rotation than the corresponding saturated bodies, so that it will probably be possible to determine whether a body is unsaturated or not by measuring its molecular rotation.

By taking into consideration the general results obtained, it is possible to deduce the magnetic rotary power of the elements when in combination. Thus, knowing the magnetic rotary power of heptane which is 7.669, and that of the CH_2 group which is 1.023, the value of 2H will be obtained by subtracting $\text{CH}_2 \times 7$ ($= 1.023 \times 7$) from C_7H_{16} ($= 7.669$), thus :

Heptane, C_7H_{16}	7.669
$\text{CH}_2 \times 7 = 1.023 \times 7$	7.161
		<hr/>
		0.508 = 2H .

Taking from the value of CH_2 that of 2H we should get that of $\text{C} = 0.515$. "Also if the value of a paraffin containing an even number of carbon atoms be divided by 2, the product should represent the value of an alcohol radical, thus :

"Hexane $= 6.646 \div 2 = 3.323$, which is the value of propyl, and if this be subtracted from a corresponding paraffin, we again get a value for hydrogen $= 0.254$.

"Having obtained these results, values for the halogens can be obtained, thus :

Propyl chloride	5.056
Propyl	3.323
		<hr/>
		1.733 = Cl.
Propyl bromide	6.885
Propyl	3.323
		<hr/>
		3.562 = Br.
Propyl iodide	11.080
Propyl	3.323
		<hr/>
		7.657 = I."

In similar ways the values of oxygen, when contained in a compound as hydroxyl and as carbonyl, are deduced. The interesting point is noticed that oxygen, as in hydroxyl in alcohols, gives a value 0.194, but in acids 0.137. The author then observes: "The variations of the magnetic rotations of substances are evidently due to differences in the molecular arrangements of the elements they contain, as well as to their composition. This is one of the most interesting points connected with this inquiry, no other physical properties of bodies yet examined showing this in such a marked manner, and it is believed that the examination of the magnetic rotation of bodies will be of considerable value to chemists in helping them to come to conclusions as to the constitution and composition of compounds under examination."

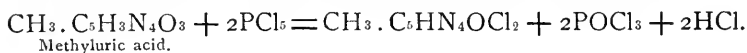
In conclusion, the author says : "There are other points connected with this paper, such as the difference in rotation between saturated and unsaturated compounds, methyl derivatives, etc., which might be summarised, but in the present state of the inquiry it is perhaps best to leave them as they are in the body of this paper. There are many other series of bodies containing other elements than those referred to in this paper, which require examination. Several of these I am making arrangements to commence the study of, such as nitrites and the nitro-compounds, also the nitrates. The subject of physical isomerides, which was the cause of my commencing the study of the magnetic rotation of bodies, is also in hand, as well as the series of aromatic compounds."

I. R.

RECENT RESEARCHES ON URIC ACID.

Notwithstanding the fact that a great deal of excellent work has been done on uric acid by Liebig and Wöhler, Baeyer, Strecker and others, the substance has up to the present been counted among the unsolved problems of chemistry. Many suggestions have been made regarding its constitution, but, owing to the lack of sufficient experimental evidence, no one of the formulas proposed has been generally accepted.

In two extremely interesting papers recently published, E. FISCHER¹ describes the results of new experiments on the subject, and suggests a formula for the acid which he considers to be in perfect harmony with all the facts known. He started with methyluric acid, which was made by heating neutral lead urate with methyl iodide at 100°. The preparation was made in a chemical factory, and the product obtained consisted of a mixture of dimethyluric acid, and probably two monomethyluric acids. This mixture was treated with phosphorus pentachloride and phosphorus oxychloride, and thus converted into a substance to which the name dichloroxymethylpurin is given, the formula of which is $\text{CH}_3 \cdot \text{C}_5\text{HN}_4\text{OCl}_2$. The reaction involved is thus expressed :



In the new chloride the remaining hydrogen atom can be replaced by methyl, and the two chlorine atoms by hydrogen, ethoxyl and other groups. By further treatment with phosphorus pentachloride it loses hydrogen and oxygen, and is converted into the trichloride $\text{CH}_3 \cdot \text{C}_5\text{N}_4\text{Cl}_3$, and in the trichloride the chlorine atoms can be replaced by hydrogen, oxygen, ethoxyl, amido groups, etc. All the products thus obtained may be regarded as derivatives of the hydrogen compound, $\text{CH}_3 \cdot \text{C}_5\text{N}_4\text{H}_3$, which is as yet unknown.

¹Berichte der deutschen chemischen Gesellschaft 17, 328, 1776.

To this compound the name methylpurin is given. The names of some of the derivatives examined are as follows:

$\text{CH}_3 \cdot \text{C}_5\text{N}_4\text{Cl}_3$	Trichlormethylpurin,
$\text{CH}_3 \cdot \text{C}_5\text{N}_4\text{Cl}(\text{OC}_2\text{H}_5)_2$. . .	Diethoxychlormethylpurin,
$\text{CH}_3 \cdot \text{C}_5\text{N}_4\text{H}_3\text{O}$	Oxymethylpurin,
$(\text{CH}_3)_2 \cdot \text{C}_5\text{N}_4\text{H}_2\text{O}$	Oxydimethylpurin,
$(\text{CH}_3)_2 \cdot \text{C}_5\text{N}_4\text{H}_2\text{O}_3$	Trioxydimethylpurin,
	(Dimethyluric acid).

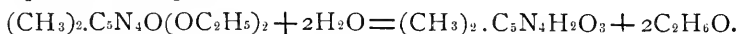
The study of the methyl derivatives of uric acid led to the most interesting results. A new methyluric acid was obtained, different from that described by Hill, and obtained by him by treating the acid urate of lead with methyl iodide. The new acid, or β -methyluric acid, was prepared by heating dichloroxymethylpurin, $\text{CH}_3 \cdot \text{C}_5\text{N}_4\text{HOCl}_2$, with hydrochloric acid at $135\text{--}140^\circ$. Nitric acid or chlorine water converts the acid into alloxan and monomethylurea; under the same treatment the isomeric or α -acid is converted into monomethylalloxan and urea. This result seems to indicate that only one of the urea residues contained in uric acid and its homologues is capable of conversion into alloxan or methylalloxan.

A dimethyl uric acid was also obtained, entirely different from that obtained by Hill, by treating lead urate with methyl iodide. The latter is designated by the author as the α -acid, the former as the β -acid. When α -dimethyluric acid is oxidised with nitric acid, or with hydrochloric acid and potassium chlorate, it breaks up, yielding monomethylalloxan and methylurea. Heated with hydrochloric acid alone the α -acid yields carbon dioxide, ammonia, methylamine and glycol, according to the following equation:

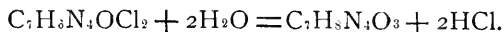


The conduct of the ammonium salt is characteristic for the acid. If a solution of the salt be boiled until the odor of ammonia is no longer perceptible, the free acid separates in fine crystals.

β -Dimethyluric acid is formed from dichloroxydimethylpurin, $(\text{CH}_3)_2 \cdot \text{C}_5\text{N}_4\text{Cl}_2\text{O}$, by treating the latter with an alcoholic solution of caustic soda, which gives the diethoxy compound, $(\text{CH}_3)_2 \cdot \text{C}_5\text{N}_4\text{O}(\text{OC}_2\text{H}_5)_2$, and then treating this with concentrated sulphuric acid, when the reaction expressed in the following equation takes place:

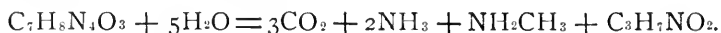


The dimethyl-acid can also be obtained by treating the dichloride with fuming hydrochloric acid at 130° . The reaction takes place thus:



The differences between the α - and β -acids are shown by the following reactions:

The ammonium salt of the β -acid is not decomposed by boiling its solution. When heated with fuming hydrochloric acid, the acid yields carbon dioxide, ammonia, methylamine and sarcosine, according to the equation:



The β -acid is oxidised as easily as the α -acid, but the products are entirely different, the chief one being a new substance, oxy- β -dimethyluric acid. When oxy- β -dimethyluric acid is heated with baryta water it yields mesoxalic acid, urea and dimethylurea. The formation of dimethylurea from β -dimethyluric acid proves that in the acid both methyl groups are united with the two nitrogen atoms which in the breaking up of β -monomethyluric acid appear in the form of monomethylurea. Further, it follows that uric acid contains two imide groups united in a urea residue, which is distinct from that part of the compound which is split off as alloxan under the influence of an acid oxidising agent.

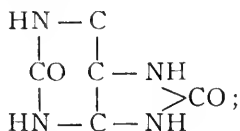
α -Dimethyluric acid could not be converted into a trimethyl derivative. The β -acid, however, yielded trimethyluric acid, which has the same composition as hydroxycaffeine, but is evidently a different compound. When the silver salt of trimethyluric acid is treated with methyl iodide, it yields tetramethyluric acid. In this acid each nitrogen atom is in combination with methyl, as is shown by treating the acid with fuming hydrochloric acid, when the nitrogen appears in the form of methylamine, no ammonia being formed. Tetramethyluric acid is isomeric with methoxycaffeine.

The principal facts upon which profitable speculation regarding the structure of uric acid can be based are the following:

1. By the direct introduction of methyl into uric acid there are formed, according to circumstances, two different monomethyl compounds. When oxidised, one of these yields methylalloxan and urea, the other yields alloxan and methylurea. From this it follows that the two urea residues in uric acid are not united in the same way with the group containing three carbon atoms.

2. In tetramethyluric acid all four nitrogen atoms are united with methyl. Hence it follows that uric acid itself contains four imide groups.

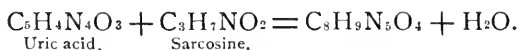
Considering these results together with the known breaking up of uric acid into alloxan and urea, we are led to the conclusion that the following group is contained in the acid:



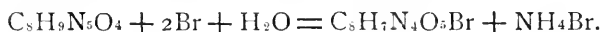
and, further, that the acid itself is properly represented by the formula:

treatment with sodium amalgam, this statement is found to be incorrect.

Another line of work which promises to lead to important results has been undertaken by F. MYLIUS.¹ This chemist starts with sarcosine-uric acid, a compound formed by heating uric acid and sarcosine together, action taking place according to the following equation :



Sarcosine-uric acid is extremely stable. It is soluble in all acids including concentrated nitric acid, and from the solutions it separates unchanged. From its solution in concentrated sulphuric acid it is thrown down by an addition of water. Bromine acts upon sarcosine-uric acid according to the equation :



The product may be regarded as sarcosine-uric acid, in which a nitrogen and a hydrogen atom are replaced by an oxygen atom, and in which besides a hydrogen atom is replaced by bromine. The acid of which the bromine compound is the monobromine substitution-product has the formula $\text{C}_8\text{H}_8\text{N}_4\text{O}_5$. If we imagine the sarcosine split off from this acid there would be left a compound of the formula $\text{C}_5\text{H}_3\text{N}_3\text{O}_5$. To this acid, although it is as yet only hypothetical, the name mesouric acid is given. The author hopes to be able to make this mesouric acid and to discover the relation existing between it and uric acid.

I. R.

BOOKS RECENTLY RECEIVED.

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- M. M. PATTISON MUIR. *A Treatise on the Principles of Chemistry.* Cambridge.
- LOTHAR MEYER. *Die modernen Theorien der Chemie. Fünfte Auflage.* Breslau.
- J. H. VAN'T HOFF. *Etudes de Dynamique Chimique.* Amsterdam.
- W. G. VALENTIN. *A Course of Qualitative Chemical Analysis. Revised and corrected by W. R. Hodgkinson and H. M. Chapman.* Sixth edition. Philadelphia.
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- W. SIMON. *Manual of Chemistry.* Philadelphia.
- T. CRANSTOUN CHARLES. *The Elements of Physiological and Pathological Chemistry.* Philadelphia.

¹Berichte der deutschen chemischen Gesellschaft **17**, 517,

AMERICAN CHEMICAL JOURNAL.

ON THE ACQUISITION OF ATMOSPHERIC NITROGEN BY PLANTS.

BY W. O. ATWATER.

The problem of the ways in which nitrogen becomes a part of living organisms, though a fundamental one in biological chemistry, cannot yet be regarded as solved. It reduces itself, however, to the question of the sources of the nitrogen of plants.

The prevalent, though not universal, opinion among chemists and vegetable physiologists appears to be that the free nitrogen of the air is not assimilated by plants, and that the proportions of combined nitrogen (ammonia, and nitric and nitrous acids) in the atmosphere are so minute that the amounts which ordinary plants could absorb during their growth must be unimportant. It is hence inferred that plants obtain no considerable part of their nitrogen directly from the air, through their leaves, and that nearly or quite all must come to them in nitrogen compounds from the soil through their roots.

There are, however, a number of considerations in the way of an unreserved acceptance of this view. It is very difficult to explain how certain plants, the legumes especially, obtain their nitrogen, if not from the air. That plants may not assimilate considerable quantities of nitrogen compounds from the atmosphere is not absolutely proven. In the classic experiments of Boussingault and of Lawes, Gilbert and Pugh, which are commonly

regarded as most decisive against the assimilation of the uncombined nitrogen of the air, the plants had, in the majority of the instances, very inadequate supplies of food, and the arrangements were such as may perhaps have excluded the action of electricity, which, as recent experiments by Berthelot imply, may effect the assimilation of free nitrogen.

The following experiments indicate that some plants, at any rate, may, when grown under normal conditions, obtain in some way and assimilate large quantities of atmospheric nitrogen.

The principal question proposed for study was this :

May plants, grown under normal conditions, acquire any considerable amount of nitrogen, free or combined, from the ambient atmosphere ?

After a series of trials had shown a not inconsiderable acquisition of atmospheric nitrogen, a second series was planned to verify the results of the first and to include a collateral inquiry :

How is the acquisition of nitrogen from the atmosphere affected by abnormal conditions of growth, and what bearing may the results obtained have upon the interpretation of those obtained by other experimenters, and upon the general question of the assimilation of atmospheric nitrogen by plants ?

PLAN OF THE EXPERIMENTS.

The experiments were made by growing peas in sand which had been purified by washing and igniting,¹ and to which were applied nutritive solutions containing known quantities of nitrogen. The amounts of nitrogen supplied in nutritive solutions and seed were compared with the amounts found at the end of the experiment in residual solution and plants. The excess of the latter amount over the former, in some cases very large, must represent nitrogen acquired, in some way, from the atmosphere.

The conditions of growth were varied in the second series :

1st. By varying the concentration of the nutritive solutions from one part by weight of dissolved salts to five or six in one thousand of solutions. (One part per thousand has, in other experiments, been found most favorable to normal growth, while two parts or more per thousand have been observed to retard or prevent assimilation and growth.²)

¹ See Appendix.

² See remarks concerning Table II, beyond.

2d. By varying the total quantity of food supplied to the roots by the solutions, from an amount seemingly sufficient, or nearly so, for normal growth, to a very scanty supply.

3d. By varying the proportion of nitrogen in the solution, making it in some cases rather small, in others very small as compared with the amount of mineral food. In this way the plants were enabled to make some growth at the expense of the nitrogen furnished to the roots, and left to gather the rest of their nitrogen, if they should so choose, from the air.

For pots in which to cultivate the plants, ordinary glass bottles of from one to three litres capacity were employed. The bottom of each was cut off and the bottle turned neck downwards. A watch glass was then inverted over the neck and the sand poured in. The pots were enclosed in wooden boxes so constructed as to exclude the light, and at the same time to permit a glass beaker to be placed under the bottle to catch any solution or sand which might accidentally run through. This simple and inexpensive arrangement served its purpose most satisfactorily, an especial advantage seeming to me to be the ease with which the water supply is regulated so as to keep the sand nearly saturated without preventing the circulation of air through it.

The nutritive solutions were such as are ordinarily used in water and sand culture. They contained potassium and calcium nitrates, potassium phosphate, magnesium sulphate and ferric chloride. The water used for the nutritive solutions, for watering the plants, and for separating the plants and residual solutions from the sand at the end of the experiments, was carefully freed from nitrogen compounds.¹ The plants were grown in the open air, but protected from rain and dew by being put under cover at night and in rainy weather. The nitrogen in seeds and in plants was determined by the soda-lime method, that in the nutritive solution by the method of Schulze-Tiemann. The only considerable source of error in the experiments seemed to be in a probable loss of nitrogen, perhaps by decomposition of the nitrates in presence of germinating seeds, as observed by Boussingault,² though possibly from decomposition of the seeds during germination and growth, especially in the trials in which the solutions were concentrated. This would tend to reduce the amount of nitrogen found at the end of the

¹ See Appendix.

² *Ann. chim. Phys.* [5] **22**, 1881, 433.

experiment, and thus make the apparent gain of nitrogen less than the amount actually acquired by the plants from the atmosphere.

Two series of experiments were made, both with peas of the "dwarf" variety called "Early Philadelphia." The first was tentative, but showed in every case an excess of nitrogen at the end of the experiment over that contained in solution and seed. The experiments of the second series were more detailed, and gave larger gains of atmospheric nitrogen.

EXPERIMENTS WITH PEAS. FIRST SERIES.

The plants of this series were grown in a greenhouse. The solution used was essentially the same as employed by Fittbogen in sand culture.¹ Instead, however, of the usual concentration 1 : 1000, it was found more convenient to prepare solutions of the concentration of 1 : 100, and dilute them as used. For this purpose the salts were dissolved in two or more separate portions to avoid precipitation. Thus in the First Series, "Solution I" contained potassium phosphate and nitrate, and "Solution II" calcium nitrate and magnesium sulphate, while ferric chloride was applied separately. The seeds, previously sprouted, were put in the sand March 26th. Solutions I and II were applied at the same time, water being added to dilute the solutions, and water was applied at intervals during growth to replace that withdrawn by the plants and by evaporation from the solution. The water-holding capacity of the sand, previously tested, was such as to permit the dilution of the solution to considerably over one thousand parts of water to one of salts. At the outset nearly as much water was added as the sand would hold, but during growth there were probably times when the solutions were so concentrated by evaporation as to make the proportion of dissolved salts much more than 1 : 1000.

With these preliminary statements, the statistics of the experiments, given in Table I herewith, will be easily understood.

TABLE I.—EXPERIMENTS WITH PEAS. FIRST SERIES.

Statistics of Seed, Solutions, Planting, Produce, etc.

Number of Exp't.	Date of Planting.	Weight of Sand.	Number of Seeds.	Weight of Seeds.	Solution I Added.	Solution II Added.	Total Solution Added.
A	March 26	2.5 kilos	6	1.4829 grams	40 cc.	40 cc.	80 cc.
B	"	2.5 "	4	1.0927 "	60 cc.	60 cc.	120 cc.
C	"	2.5 "	4	1.0675 "	40 cc.	40 cc.	80 cc.

¹Versuchs-Stationen, 13, 81.

Number of Exp't.	Date of Harvesting.	Number of Plants Matured.	Average Height of Plants.	Number of Peas.	Weight of Vines, Leaves, Fruit, etc.	Weight of Roots and Adhering Sand.	Total Weight of Plants.
A	May 27	6	60 cm.	18	6.9 grams.	4.9 grams.	11.8 grams.
B	June 7	4	77 "	16	5.8 "	5.2 "	11.0 "
C	May 27	4	70 "	12	4.3 "	14.5 "	13.8 "

Nitrogen Statistics.

Number of Exp't.	Nitrogen supplied at beginning of Experiment.			Nitrogen found at End of Experiment.			Gain of Nitrogen.
	In Seed.	In Nutritive Solution.	Total.	In Residual Solutions.	In Plants.	Total.	
A	49.5 mgr.	61.4 mgm.	110.9 mgm.	7.2 mgm.	167.2 mgm.	174.4 mgm.	63.5 mgm.
B	36.4 "	92.2 "	128.6 "	8.0 "	133.8 "	141.8 "	13.2 "
C	35.6 "	61.4 "	97.0 "	1.3 "	108.7 "	110.0 "	13.0 "

Besides the Nos. A, B and C, the series included two others, D and E, into which, unfortunately, a quantity of rain-water fell through a leak in the roof of the greenhouse during a violent shower. The water percolated through the sand and was caught in the beakers below. The accident was discovered by the gardener who had been charged to watch the plants, and who poured the contents of the beakers back upon the sand before either the assistant in charge of the experiments or myself had learned of the matter. One of the pots received more rain-water than the other, and more fell into the beaker below. The analysis at the end of the experiment showed in one case a loss of nitrogen and in the other a very large gain. The average of the two gives a gain of nitrogen not widely different from the average gain in the other three, A, B and C. It seems to me very probable that in pouring the percolated solution back into the pots the gardener may have changed the beakers, emptying that under pot D into pot E, and *vice versa*. If so, this would readily account for the discrepant results in D and E. The nitrogen statistics of these are as follows:

Number of Exp't.	Nitrogen supplied.			Nitrogen found.			Gain + or Loss of Nitrogen.
	In Seed.	In Solution.	Total.	In Plant.	In Residual Solution.	Total.	
D	16.66 mgm.	92.17 mgm.	108.83 mgm.	94.19 mgm.	3.10 mgm.	97.29 mgm.	-10.15 mgm.
E	15.25 "	61.44 "	76.69 "	82.52 "	56.82 "	139.34 "	+62.65 "
D + E	31.91 "	153.61 "	185.52 "	176.71 "	59.92 "	236.63 "	+52.50 "

It would, of course, be unwarrantable to include these experiments with those described above (A, B and C), and, for that matter, the possibility of such an accident casts a suspicion upon the whole series, so that their results can be entitled to full credence only on condition of their being verified by repetition under circumstances fitted to preclude such sources of error. Nevertheless, the facts that the trials in which there were no apparent sources of uncertainty showed large gains of nitrogen, amounting in A to 38 per cent. of the total nitrogen of the plants, and that the average of C and D tallies with that of A, B and C, hardly leave room for doubt that the plants did somehow obtain a considerable portion of their nitrogen from the air. The results thus obtained seemed, therefore, to warrant farther and more detailed experiments.

EXPERIMENTS WITH PEAS. SECOND SERIES.

Accordingly, the following spring, a small building was erected and provided with large doors and movable tables, upon which the plants could stand, and be moved out and in at will. The immediate care of the experiments was entrusted to an assistant, who lived close by, and whose duty included moving the plants into the open air in the morning and back under cover at night and whenever there was a prospect of rain. The plants were thus carefully and constantly watched and protected from rain and dew.

The general arrangement of the experiments was similar to that of the first series. The nutritive solutions were prepared by dissolving each salt separately. The separate solutions were as follows, each containing (approximately) 1 gram of the water-free salt in 100 cc.:

Solution "NI," $\text{Ca}(\text{NO}_3)_2$.

Solution "NII," KNO_3 .

Solution "NIII," $\text{Ca}(\text{NO}_3)_2 + \text{KNO}_3$ (NI and NII mixed).

Solution " P_2O_5 ," K_2HPO_4 .

Solution "Mg," MgSO_4 .

Solution "Fe," Fe_2Cl_6 .

All the pots received like quantities of Solutions " P_2O_5 ," "Mg" and "Fe." One half, Group I, six pots, received nitrogen in Solution "NI." The other half, Group II, six pots, received

nitrogen in Solutions "NI" and "NIII." The mixture given to Group I was called the "Smaller Nitrogen Ration"; that of Group II, the "Larger Nitrogen Ration." One-third of the pots had 1 kilogram of sand, one-third 2 kilos, and one-third 3 kilos, each. One half of the pots of each group had three plants, the others six plants each. The arrangements and results of the experiments appear in the tables of statistics herewith.

TABLE II.—EXPERIMENTS WITH PEAS. SECOND SERIES.

Statistics of Seed, Solutions, Planting, etc.

	Number of Experiment.	Date of Planting.	Weight of Sand.	Number of Seeds.	Weight of Seeds.	Amounts of Solutions added (one-half each March 30, the rest May 29.)*						Amount of Water Added.
						NI.	NIII.	P ₂ O ₅ .	Mg.	Fe.	Total.	
Group I. Smaller Nitrogen Ration.	1	March 30	kilos		grams.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
	3	"		3	0.8707	50	50	30	20	1	101	2599
	5	"		3	1.7237	50	50	30	20	1	101	2599
	7	"		3	0.8117	50	50	30	20	1	101	2849
	9	"		3	1.6973	50	50	30	20	1	101	2849
	11	"		3	0.8379	50	50	30	20	1	101	3099
	11	"		3	1.7219	50	50	30	20	1	101	3099
Group II. Larger Nitrogen Ration.	2	"		3	0.8165	50	50	30	20	1	151	2574
	4	"		3	1.7849	50	50	30	20	1	151	2574
	6	"		3	0.8258	50	50	30	20	1	151	2824
	8	"		3	1.6685	50	50	30	20	1	151	2824
	10	"		3	0.8214	50	50	30	20	1	151	3074
	12	"		3	1.6337	50	50	30	20	1	151	3074
	12	"		3	1.6337	50	50	30	20	1	151	3074

	Number of Experiment.	Date of Harvesting.	Number of Matured Plants.	Average Height of Plants.	Number of Pods.	Number of Perfect Peas.	Number of Rudimentary Peas.	Weight of Vines, Foliage and Fruit.	Weight of Roots and Adhering Sand.	Total Weight of Plants and Adhering Sand.
								grams.	grams.	grams.
Group I. Smaller Nitrogen Ration.	1	July 3	3	cm.	5	12	4	5.5	12.9	18.4
	3	"	3	38	10	13	4	6.8	4.9	11.7
	5	"	3	45	7	17	6	7.0	17.7	24.7
	7	"	3	35	12	15	8	6.4	21.4	27.8
	9	"	3	40	7	23	1	7.3	19.0	26.3
	11	"	3	68	14	23	6	8.8	24.2	33.0
	11	"	3	68	14	23	6	8.8	24.2	33.0
Group II. Larger Nitrogen Ration.	2	"	3	50	8	19	6	6.8	5.2	12.0
	4	"	3	62	12	23	5	8.0	5.5	13.5
	6	"	3	40	7	20	4	6.9	19.4	26.3
	8	"	3	33	12	20	7	7.6	17.4	25.0
	10	"	3	50	7	18	2	7.4	19.6	27.0
	12	"	3	45	9	15	6	8.0	10.7	18.7
	12	"	3	45	9	15	6	8.0	10.7	18.7

* Except that the whole of solution "Fe" was added March 30.

† Only five plants matured.

Nitrogen Statistics.

	Number of Experiment	Nitrogen supplied at beginning and during Experiment.			Nitrogen found at End of Experiment.			Gain + or Loss — of Nitrogen.
		In Seeds.	In Solutions.	Total.	In Vines, Roots, etc.	In Residual Solutions.	Total.	
Group I. Smaller Nitrogen Ration.	1	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
	3	36.7	59.4	96.1	116.4	1.4	117.8	+ 21.7
	3	72.6	59.4	132.0	158.9	3.8	162.7	+ 30.7
	3	34.2	59.4	93.6	156.1	1.0	156.1	+ 62.5
	9	71.5	59.4	130.9	158.1	0.0	158.1	+ 27.2
	11	35.3	59.4	94.7	186.5	1.4	187.9	+ 93.2
		72.5	59.4	131.9	210.9	2.7	213.6	+ 81.7
Group II. Larger Nitrogen Ration.	2	34.4	136.9	171.3	178.9	2.0	180.9	+ 9.6
	4	75.2	136.9	212.1	200.6	12.8	213.4	+ 1.3
	6	34.8	136.9	171.7	149.6	1.2	150.8	- 20.9
	8	70.3	136.9	207.2	197.5	12.7	210.2	+ 3.0
	10	34.6	136.9	171.5	277.8	35.7	313.5	+ 142.0
	12	68.8	136.9	205.7	260.2	45.7	305.9	+ 100.2

Concerning the data in Table II the following statements may be made:

1. The seeds were planted March 30th, and the plants harvested July 3d. The plants were ripe, however, and watering ceased some time before the harvesting could be done, so that I do not think the actual period of active growth should be taken at over 72 days.

2. As three kilograms of sand held more solution than one, while the amounts of dissolved salts were the same, the concentration of the solutions differed widely. The amounts in each case varied somewhat with evaporation and watering. The solutions in the 3 kilos of sand contained generally from 0.8 to 1.6 grams, or thereabouts, of dissolved salts in 1000 cc. and were thus tolerably dilute. Those in 1 and 2 kilos of sand contained from 2.5 to 6 parts of salts per 1000, and were hence very concentrated.* It has been shown by Nobbe¹ and others that though many of our cultivated plants may endure very concentrated solutions, yet if the concentration be sufficiently great or protracted, assimilation may be hindered and the development of the plants retarded or stopped. Thus Nobbe and Siegert found a concentration of 3 or even 2 per mille, *i. e.* 3 or 2 parts of salts in 1000 of solution, prejudicial to the growth of buckwheat and barley plants; and the general result of experiments on the growth of these plants in aqueous solutions indicates that a concentration of 1 per mille is

¹ Landw. Vs. Stationen, 6, 17, and 8, 337.

perhaps the most favorable to normal growth. A still greater dilution has, I believe, been found requisite for some leguminous plants. Accordingly we have in Nos. 1 to 8 a concentration unfavorable, and in Nos. 9 to 12 one tolerably well adapted to normal growth.

3. The amount of food in the solutions was estimated to be rather small for three plants, and made of course a very scanty supply for six. Accordingly Nos. 3, 4, 7, 8, 11 and 12 were very insufficiently, and Nos. 1, 2, 5, 6, 9 and 10 tolerably well fed.

4. The amounts of mineral food were the same for all. "The larger nitrogen ration" was calculated to supply an amount of nitrogen rather small in proportion to the mineral food, 140 mgms. in each case. "The smaller nitrogen ration" contained less than half as much nitrogen, 60 mgms. in each case.

We have thus, in the experiments of the Second Series, the variations in concentration of solutions, total food-supply, and supply of nitrogen, referred to above, as provided to test the effects of normal and abnormal conditions upon the assimilation of nitrogen.

We may place the principal data of Tables I and II together in such a way as to show more clearly the amounts of nitrogen supplied and found, as is done in Table III.

TABLE III.—NITROGEN STATISTICS OF THE EXPERIMENTS.

	Number of Experiment.	Kilos of Sand used.	Number of Plants.	Nitrogen supplied to Plants by Solution and Seed.*	Nitrogen contained in Plants	Gain +, or Loss — of Nitrogen, <i>i. e.</i> , excess in Plant above that supplied by Solution and Seed.		
						Total Gain or Loss.	Gain or Loss in per cent.	
							Of Nitrogen supplied by Solution and Seed.	Of Nitrogen contained in Plants.
Second Series.	First Series.	A	2½	6	mgm	mgm.	mgm.	per cent.
		B	2½	4	103.7	167.2	+ 63.5	+ 61.2
		C	2½	4	120.6	133.8	+ 13.2	+ 10.9
	Group I. Smaller Nitrogen Ration.				95.7	108.7	+ 13.0	+ 13.6
		1	1	3	94.7	116.4	+ 21.7	+ 22.9
		3	1	3	128.2	158.9	+ 30.7	+ 23.9
		5	2	3	93.6	156.1	+ 62.5	+ 66.8
		7	2	3	130.9	158.1	+ 27.2	+ 20.8
		9	3	3	93.3	186.5	+ 93.2	+ 99.9
		11	3	6	129.2	210.9	+ 81.7	+ 63.2
								+ 38.6
	Group II. Larger Nitrogen Ration.	2	1	3	169.3	178.9	+ 9.6	+ 5.6
		4	1	6	199.3	200.6	+ 1.3	+ 5.7
		6	2	3	170.5	149.6	— 20.9	— 12.3
		8	2	6	194.5	197.5	+ 3.0	+ 1.5
		10	3	3	135.8	277.5	+ 142.0	+ 104.5
		12	3	6	161.0	260.2	+ 99.2	+ 62.0
								+ 51.1
								+ 38.1

* Computed by adding the nitrogen of nutritive solution and seed, and subtracting that of residual solution. This is subtracted from the nitrogen in the plants, and the difference called "Gain or Loss." Any loss of nitrogen during the experiment, by decomposition or otherwise, would thus diminish the calculated gain of nitrogen.

RESULTS OF THE EXPERIMENTS.

Of eight trials in concentrated solutions, Nos. 1-8, one showed a small loss, and the rest more or less gain of nitrogen. I do not know how to explain the loss of nitrogen, unless it be by decomposition of either the nitrates in the presence of germinating seeds, as shown by Boussingault (see above), or the nitrogenous compounds of the seeds, or both. If such decomposition took place, it may, for aught I can say, have occurred in the dilute solutions also.

In the moderately dilute solutions, Nos. 8-12, in which the concentration was such as has elsewhere been found favorable to healthy growth, the nitrogen of the plants largely exceeded that furnished by nutritive solution and seed. This appears more clearly when the figures are arranged as below.

ATMOSPHERIC NITROGEN ACQUIRED BY PLANTS GROWN IN MODERATELY DILUTE SOLUTIONS.

	Gain of Nitrogen.			
	In Milligrams per Experiment.		In per cent. of Total Nitrogen of Plants.	
	With smaller Nitrogen Ration.	With larger Nitrogen Ration.	With smaller Nitrogen Ration.	With larger Nitrogen Ration.
With six plants, <i>i. e.</i> smaller food supply..	81.7 mgms.	99.2 mgms.	38.7 per ct.	38.1 per ct.
With three plants, <i>i. e.</i> larger food supply..	93.2 "	142.0 "	50.0 "	51.1 "

That is to say, in the four trials with solutions sufficiently dilute to permit normal assimilation, the very poorly-fed plants obtained over one-third, and the tolerably well-fed ones one-half of their whole nitrogen from the atmosphere. The plants acquired a milligram of nitrogen from the air, for every milligram taken from solution and seed. And what is even more noticeable, they did this, not only where the amount of nitrogen supplied was very small, but also where it was more than twice as large.

As stated elsewhere, the apparent sources of error were all such as to diminish the nitrogen found at the end of the experiment. The apparent gain of nitrogen therefore could have been no more, and may have been less than the actual gain. Furthermore, the food-supply, even in the most favorable cases, was evidently smaller than the plants needed for their best development, since

even the best-fed plants appeared rather stunted. In later trials made to test this special question of the effect of food-supply, peas were supplied with solutions of the same composition and concentration as those which gave the best results above, but in much larger quantity. The result of this larger food-supply was a much more vigorous growth. The natural inference is, that if the peas which had the largest supply of food and acquired the most nitrogen from the air had been still better fed, they might have assimilated as much or more atmospheric nitrogen.

As regards the effects of the three factors, concentration of nutritive solution, total food supply, and supply of nitrogen, the results show very clearly that the assimilation of nitrogen decreased as each was made abnormal, and increased as each became more nearly normal.

The quantity of nitrogen acquired from the atmosphere appears still more strikingly if we compare it with the quantities contained in plants as commonly cultivated. The superficial area of the pots in which these plants grew was about 104 square centimetres. Remembering that one miligram per square decimetre corresponds to one kilogram per hectare, and 1.12 kilos per hectare to 1 pound per acre, and taking for the average percentages of nitrogen in field crops those given in Wolff's tables (Mentzel und V. Lengerke, Landw. Kalender, 1884), we have the following figures :

COMPARISON BETWEEN THE AMOUNTS OF ATMOSPHERIC NITROGEN ACQUIRED BY THE EXPERIMENTAL PLANTS AND THE TOTAL NITROGEN OF PLANTS IN ORDINARY CULTURE.

	Nitrogen.					
	Per experiment.		Per hectare.		Per acre.	
	Contained in Plants.	Acquired from Air by Plants.	Contained in Plants.	Acquired from Air by Plants.	Contained in Plants.	Acquired from Air by Plants.
<i>Plants in Dilute Solutions.</i>						
Smaller ni- { Smaller food supply.....	mgm. 210.9	mgm. 81.7	kilos. 202.9	kilos. 78.6	lbs. 181.4	lbs. 70.3
trogen ration. } Larger total food supply.	186.5	93.2	179.4	89.7	160.4	80.2
Larger nitrogen } Smaller food supply....	260.2	99.2	250.3	95.4	223.8	85.3
ration. } Larger food supply.....	277.8	142.0	267.2	136.6	238.9	122.1
Average of experiments with dilute solutions	233.9	104.0	225.0	100.0	201.1	89.5
<i>Plants in Field Culture.</i>						
Wheat, 30 bushels (1800 lbs.) per acre....			66.1		59.0	
Hay (mixed grasses), 5000 lbs. per acre..			86.8		77.5	
Clover hay, 6000 lbs. per acre.....			132.8		118.6	

In the experiments in which the conditions of growth were approximately normal, the excess of nitrogen in the plant over that supplied by nutritive solution and seed averaged 90 pounds per acre or 100 kilos per hectare; while in the single one where there was no considerable apparent hindrance to normal growth, that with three plants and the larger nitrogen ration, it rose to 122.1 pounds per acre, or 136.6 kilos per hectare, twice as much as the total nitrogen in grain and straw of a wheat crop of thirty bushels, and more than the total nitrogen of three tons of clover hay. And this remarkable gain cannot represent more, and may be less, than the actual quantity of atmospheric nitrogen which the plants acquired during their brief period of seventy-two days of growth.

DISCUSSION OF THE RESULTS.

This nitrogen must have been either absorbed by the foliage of the plants, or first taken from the air by the nutritive solutions, and thus communicated to the plants through their roots. If it came by the latter route, it was probably as combined nitrogen, ammonia, nitrates or nitrites.

Was the atmospheric nitrogen absorbed directly by the foliage of the plants, or was it first absorbed by the nutritive solutions and thus communicated to the plants through their roots?

In order to eliminate the uncertain factor of absorption of nitrogen compounds through the roots of the plants, a series of experiments was devised to admit only air freed from nitrogen compounds to contact with the nutritive solutions, the foliage remaining in open air. These unfortunately failed of completion, and I have since found no opportunity to repeat them, though I hope hereafter to do so.

During the course of the experiments of the second series, a number of pots with sand and solutions like those in which the plants grew were kept alongside the latter. The solutions at the end of the experiments revealed only such minute quantities of combined nitrogen as are commonly found in natural waters exposed to the air. That these solutions, without plants, had so little of nitrogen compounds, is, however, no proof that the solutions in which the plants grew might not have yielded to the plants some of the ammonia which they were continually absorbing, and

which, if not somehow seized upon, would escape by virtue of its tension. The fact that the solutions in which the plants grew were neutral or faintly alkaline, would, however, make the hypothesis of any considerable absorption of ammonia apparently improbable. It is worth noting, too, that the residual solutions at the end of the experiment contained only the minutest quantities of ammonia discernible by aid of Nessler's reagent.

The only experiments with which I am familiar, bearing directly upon this problem, are those of Heinrichs¹ and Schlössing.² These were made to determine the maximum amounts of combined nitrogen which could be absorbed from the atmosphere under the most favorable circumstances. Heinrichs exposed dilute acid, and Schlössing a moist, acid, porous soil to the air, protecting them, however, from rain and dew. Heinrichs' experiments continued through two years; Schlössing's during shorter periods in the summer months. The absorption of atmospheric nitrogen was greatest in summer and least in winter. For the period of my experiments, 72 days in April, May and June, according to my computation, the amount of nitrogen absorbed as ammonia by dilute acid was practically identical with that absorbed as ammonia, and nitric and nitrous acids by the soil, to wit, 9.8 mgms. per square decimetre (kilos per hectare); but the amounts of nitric and nitrous acids in the atmosphere are very small, and, as has been noted, especially by Schlössing, these are brought to the earth by rain and other aqueous deposits, from which ammonia, by virtue of its tension, more readily escapes and is thus left in the air. Schlössing determined, furthermore, the nitric and nitrous acids as well as the ammonia absorbed.

The solution in which my plants grew was, like the soil and acid solutions above, protected from rain and dew, and was neutral or faintly alkaline. It would seem that they could hardly have absorbed as much of nitrogen compounds from the air as an acid solution. That they could have both absorbed and communicated to the plants so much combined nitrogen is still harder to believe. But allowing that the plants in these experiments could have obtained in this way as much nitrogen as was absorbed by the acid solutions or soil in the experiments of Heinrichs and Schlössing, to wit, 10 kilos per hectare, we should even then have, in the case in which

the growth appears to have been most nearly normal, that with three plants, in the dilute solution, with the larger nitrogen ration :

Minimum amount of atmospheric nitrogen			
acquired by plants,	.	.	137 kilos per hectare.
Maximum amount of atmospheric nitrogen			
conveyed to plants by solution,	.	.	10 " "
<hr/>			
Balance, minimum acquired by foliage,	.	127	" "
Balance in per cent. of total atmospheric			
nitrogen,	.	.	93 per cent.
Balance in per cent. of total nitrogen of			
plants,	.	.	47 "

That is to say, if it be correct to assume that the neutral or faintly alkaline nutritive solutions here could have been absorbed from the air and communicated to the roots no more nitrogen than the maximum amount found to be absorbed elsewhere under the most favorable conditions for absorption, namely, by an acid solution, or a moist, acid, porous soil, we have, in the case in which the conditions of assimilation were most nearly normal, an amount of nitrogen in the plants which they could have obtained from no other source than the atmosphere, and through no other channel than their foliage, and which could not have been less, and was probably more than 47 per cent. of the total nitrogen of the plant, and corresponded to 127 kilos per hectare (113 pounds per acre).

Was the atmospheric nitrogen acquired by the plants in the form of combined nitrogen?

If this nitrogen was acquired by the foliage, it must have been either free or combined nitrogen. The supposition that the plants could have acquired so much combined nitrogen from the air would seem to me very improbable.

The theory has been proposed by Grandeau¹ that the leaf, containing acid juices, "acts like an acid, watery medium, absorbing ammonia like an acid solution," and that plants may in this way acquire considerable quantities of combined nitrogen from the air. The amount of leaf surface of the plants in these experiments was not estimated. The plants were, however, small even for dwarf

¹ Nutrition de la Plante, pp. 574-578.

peas. In a later trial the area of the full-grown leaves in a duplicate of the experiment which gave the largest nitrogen assimilation, was computed at not over 320 cm. at the outside (assuming the surface to be smooth), which would make for the two surfaces 640 cm. or about six times the superficial area of the medium in which the plants grew. The maximum absorption of ammonia by an acid solution of this surface during the period of growth of the plants was computed above at a little less than the equivalent of 10 kilos of nitrogen per hectare. If, now, we assume that the tissues enclosing the juices offer no resistance to the passage of ammonia, and that the leaf acts as an "acid, watery medium, absorbing ammonia like an acidified solution," and if we go still further, and allow the absorption to have been as great during the whole period of growth as would correspond to the double surface of the full-grown leaves; and if, finally, we allow this absorption to be equivalent to the maximum observed elsewhere, we should, even then, have an absorption equivalent to only 60 kilos per hectare, which, added to the maximum possible absorption for the solution as above estimated, would make only 70 kilos, while the plants somehow acquired a minimum of 137 kilos per hectare.

But the best information at hand¹ forbids the assumption that the juices are uniformly or even generally acid; of the permeability of the leaf tissues to gases we have little certain knowledge; the leaves had their full size during only the latter part of the period of growth; in short, it would require a considerable stretch of the imagination to assume any such absorption as that just calculated. Crude and unreliable as these estimates are, they nevertheless make it very difficult to conceive how such very large quantities of nitrogen as these plants obtained could have been absorbed as nitrogen compounds by their foliage from the air.

Of course, the amount of combined nitrogen which the plants could have obtained in this way is a matter to be settled by experiment, and the considerations just presented may be superfluous. Instead of urging any views of my own, therefore, I may with greater propriety cite those of more experienced investigators.

M. Boussingault, in discussing² the sources of the nitrogen of plants, says that "Part of the nitrogen of plants comes from the

¹ *E. g. vid. Sachs Botanische Zeitung*, 1862, 257. •

² In a communication to Dr. J. H. Gilbert, *vide* paper "On some points connected with vegetation," *Am. Jour. Sci.* [3], 13, 183 (reprinted from Address delivered at South Kensington).

atmosphere, because it furnishes ammonia in the form of carbonate, nitrates or nitrites, and various kinds of dust. Theodore de Saussure was first to demonstrate the presence of ammonia in the air, and, consequently, in meteoric waters. Liebig exaggerated the influence of this ammonia on vegetation, since he went so far as to deny the utility of the nitrogen which forms a part of farm-yard manure. This influence is, nevertheless, real and comprised within limits, which have recently been indicated in the remarkable investigations of M. Schlössing."

Messrs. Lawes and Gilbert, in an extended discussion of this subject, remark as follows¹ (the italics are my own):

"One view which has been advocated is, that broad-leaved plants have the power of taking up combined nitrogen from the atmosphere, in a manner or in a degree not possessed by the narrow-leaved, gramineous plants. The only experiments that we are aware of, made to determine whether plants can take up nitrogen by their leaves from ammonia supplied to them in the ambient atmosphere, are those of Adolph Mayer² in Germany, and of Schlössing³ in France. Both found that very small quantities of nitrogen were so taken up; but both concluded that the action takes place in very immaterial degree in natural vegetation. We have elsewhere shown that not only a consideration of the chemistry and the physics of the subject would lead to the conclusion that the plants which assimilate more nitrogen over a given area than others, do not do so by virtue of a greater power of absorbing already combined nitrogen from the atmosphere, by their leaves; but apart from such considerations, our statistics of nitrogen production *seem to preclude the idea that the broad-leaved root crops, turnips and the like, to which the function has with the most confidence been attributed, take up any material proportion of their nitrogen by their leaves from combined nitrogen in the atmosphere.*"

¹ "Determination of Nitrogen Soils," London Edition, p. 21.

² It is, nevertheless, worth noting that in Mayer's experiments (Landw. Vs. Stationen, 17, 359), the plants had for the most part little or no nitrogen at the disposal of their roots, except that supplied by the seed, that the other conditions of growth were more or less abnormal, and that in consequence the plants were stunted and sickly. While therefore they render Mayer's conclusion probable, they do not seem to me decisive.

³ The experiments of Schlössing I presume to be those described in the *Comptes rendus*, 78, 1700. These were made with tobacco plants grown with the roots in a fertile soil, but with the foliage enclosed in a glass case, the air in which was artificially supplied with a very large amount of ammonia. The results show the possibility of the absorption of ammonia by the foliage, but seem to me to give very little certain indication as to the amount that may be acquired by plants under normal conditions.

And further, in recapitulating the results of their own and other experiments upon the various supposed sources of nitrogen of crops, Messrs. Lawes and Gilbert continue:¹

"It has been shown that the determined amounts of combined nitrogen annually coming down in the measured aqueous deposits from the atmosphere in the open country are entirely insufficient to do more than supply a small proportion of the nitrogen assimilated by crops so grown.

"With regard to other possible supplies of already combined nitrogen from the atmosphere to the soil, it has been pointed out that there is no quantitative evidence whatever at command, and that such evidence as does exist leads to the conclusion that such supplies are *very limited and inadequate*.

"*The same may be said, even in a greater degree, of the supposed combination of the free nitrogen of the air within the soil; also of the supposition that plants take up any material proportion of their nitrogen from combined nitrogen in the atmosphere by their leaves.*"

There is no doubt that plants do obtain some combined nitrogen from the atmosphere. But unless the decided conclusions of those who have devoted the most experimental study to the subject, as well as my own estimates above, are very far out of the way, the supposition that the plants, in the experiments here reported, could have acquired more than a fraction of their atmospheric nitrogen in this manner, would be out of the question.

Did the plants acquire free nitrogen from the atmosphere?

The only other possible hypothesis is that the plants assimilated the free nitrogen of the air. That plants assimilate free nitrogen is contrary to general belief and to the results of the best investigations of the subject. The disagreement between these results and my own may, however, be more apparent than real. Two points in particular seem to me worthy of note.

First. The plants in the experiments in which no considerable assimilation of atmospheric nitrogen has been observed had, in general, little or no combined nitrogen at the disposal of their roots save the small quantities contained in the seed. The depression of nitrogen assimilation consequent upon inadequate supply of food, especially of nitrogen, in my experiments is very marked.

¹ *Loc. cit.* p. 30.

Second. The experiments which are most decisive against the assimilation of free nitrogen, namely, those of Boussingault¹ and of Lawes, Gilbert and Pugh,² were conducted under glass covers connected with the earth. Berthelot has shown that free nitrogen may be assimilated by vegetable substances, dextrine, cellulose, etc., under the influence of electricity of a potential similar to that which obtains near the surface of the earth, in the strata of air in which our cultivated plants grow.³ The inference that the compounds in living plants may assimilate nitrogen in the same way is natural. That this electrical tension may have been absent in the experiments with the plants under glass, referred to, would seem probable. The hypothesis of the assimilation of free nitrogen by plants through the agency of electricity, and the absence of that agency in the experiments of Boussingault and of Lawes, Gilbert and Pugh, would, with the effect of scanty food supply, explain the discrepancy between their experiments and my own, in which the conditions of growth were normal, and would clear up the worst difficulty in the much vexed question of the sources of nitrogen of plants.

Of course such hypotheses can be accepted only after experimental verification. I hope that circumstances may permit the execution of some experiments which have been planned for the study of this and some of the other phases of the question.

In this connection it may not be out of place to note the observation made by Lawes and Gilbert,⁴ Dehérain⁵ and Schulz-Lupitz,⁶ that while soils in which potatoes, cereals, and other crops were cultivated grew poorer in nitrogen, the nitrogen in those on which legumes were grown, under conditions precisely similar, uniformly increased. That is to say, the leguminous plants after providing themselves with their larger amounts of nitrogen, left more nitrogen in the soil than the latter contained before. While the explanation of this fact is, doubtless, complex, and very likely involves an acquisition of nitrogen by the soil from the air, as combined nitrogen, and perhaps as free nitrogen fixed by the humus of the soil through the agency of electricity; yet it seems to me not improbable that a most important factor must be sought in a power of the plants to acquire nitrogen from the air, in which some of the legumes especially excel.

¹ Ann. ch. Phys. 1838-1855, passim.

² Phil. Trans. 1861, 2, 437.

³ Compt. rend. 82-88, passim, and in more detail in Ann. ch. Phys. [5] 10, 52, and 12, 457.

⁴ Am. Jour. Sci. [3] 13, 28. ⁵ Ann. Agronom., 1882, 322. ⁶ Ct. bt. f. Ag. Chem., 1883, 145.

IN CONCLUSION.

The outcome of these experiments may be concisely stated thus :

1. The plants, peas, grown in nutritive solutions exposed to the air, but protected from rain and dew, contained at maturity much more nitrogen than was supplied them in nutritive solution and seed. Such were the results of a first series of trials, confirmed, even more strikingly, by a second series the succeeding year. For this excess of nitrogen there was but one possible source, namely, the atmosphere.

2. The conditions of growth were varied by varying (1) the concentration of the nutritive solutions, (2) the total amount of food, and (3) the amount of nitrogen in the nutritive solutions. In each case the gain of nitrogen was largest when the conditions of growth were most nearly normal, and smaller as either condition was made abnormal. Thus the gain was small where the solutions were very concentrated, and largest where the concentration was such as has generally been found favorable to normal assimilation and growth. The amount of nitrogen acquired from the atmosphere rose and fell with the amount of food at the disposal of the roots, being largest where the plants were tolerably well fed, and smallest where the food-supply was inadequate. So, likewise, where the supply of nitrogen varied, the amount of mineral food remaining the same, the plants acquired more or less aerial nitrogen in proportion as more or less nitrogen was supplied to them in the nutritive solution.

3. In the four trials with solutions sufficiently dilute to permit normal assimilation, the very poorly fed plants obtained one-third, and the tolerably well fed ones one-half of their whole nitrogen from the air. And what is even more noticeable, they did this not only where the quantity of nitrogen in the nutritive solution and seed was very small, but also where it was more than twice as large. When we compare the nitrogen in the experimental plants with that in plants commonly cultivated, by comparing the area of the pots in which the experimental plants grew with an acre or a hectare, it appears that, in the case in which the conditions of growth were most nearly normal, the plants acquired atmospheric nitrogen at the rate of 137 kilograms per hectare, or 122 pounds per acre, more than twice as much as the total amount contained in the grain and straw of a wheat crop of thirty bushels of grain

per acre (27 hectolitres per hectare), and more than is contained in a clover crop of 6000 pounds per acre (6720 kilos per hectare).

5. How, and in what form, this nitrogen was acquired the experiments do not tell. It must have come to the plants as either combined nitrogen, ammonia, nitric acid or nitrous acid, or as free nitrogen. It must have been either taken directly by the foliage, or first absorbed by the nutritive solution and communicated by it to roots. That the whole, or indeed any considerable portion could have been gathered from the air and conveyed to the plants by the nutritive solution, which was neutral or slightly alkaline during growth, is, to say the least, in the most direct apparent contradiction with the best experimental evidence at hand. The hypothesis of the absorption of any considerable quantity of combined nitrogen by the leaves of the plants is directly opposed, as well to the testimony of the most reliable experiments upon the subject as to the seemingly unanimous opinion of the men who have made them. The only remaining hypothesis is that of the assimilation of the free nitrogen of the air by the plants. This is likewise contrary to the results of the best investigations.

A way out of the difficulty may, perhaps, be found in the observation by Berthelot of the assimilation of free nitrogen by vegetable matters, through aid of electricity of a potential similar to that which obtains in the air near the surface of the earth; an agency which may have been excluded in the experiments which are most decisive against the assimilation of free nitrogen.

As to whether this latter hypothesis, or either of the others, is correct, I venture no opinion, deeming it wiser to abide by the simple fact that the plants acquired a considerable quantity of nitrogen from the atmosphere, and look to future research for the explanation.

I improve this opportunity to express my obligations to my assistant, Mr. C. D. Woods, by whom the details of the experiments above described have been most faithfully and skilfully performed.

It gives me great pleasure, also, to bear testimony to the generosity of Hon. J. W. Alsop, M. D., of this city (Middletown, Conn.), who has, by defraying the larger part of the pecuniary cost, and by aid in other ways, made the investigations practicable.

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APPENDIX.

The following are details of the chemical work of the experiments. It may not be out of place to say that the nitrogen determinations were made after a not inconsiderable outlay of time and labor in getting the methods well in hand.

The sand was washed with ordinary, and then with distilled water, ignited, and finally tested for nitrogen compounds by combustion with soda-lime, which revealed no nitrogen.

The water used for the solutions, for watering the plants, and for separating roots and residual solutions from sand at the end of the experiment, had been previously freed from nitrogen compounds by distilling with potassium permanganate and hydroxide, and rejecting so much of the distillate as gave a visible ammonia reaction with Nessler's reagent.

The determinations of nitrogen in the seeds and plants were made by the soda-lime method. Those of the nitrogen in the nutritive solutions employed, and in the residual solutions at the end of the experiment, were made by the method of Schulze-Tiemann.¹

It is quite possible that the plants may have contained nitrates, more or less of the nitrogen of which would escape determination by soda-lime. The error thus introduced, if any, would decrease the amount of nitrogen found at the end of the experiment, and thus the apparent gain of nitrogen from the air.

Nitrogen in Peas. Determined by Soda-lime.

FIRST SERIES. Five peas. Nitrogen determined in each separately.

No.	Weight of pea.	N. Found.	Per cent. N.	
1.....	217.4 mgm.	6.96 mgm.	3.20	Average, 3.334 per cent. N.
" 2.....	238.7	7.83	3.28	
" 3.....	215.0	7.32	3.40	
" 4.....	206.9	6.96	3.36	
" 5.....	234.0	8.03	3.43	

SECOND SERIES. Several peas ground together, and determinations made in three separate portions of this sample.

Weight of portion.	N. Found.	Per cent. N.	
1000 mgm.	42.18 mgm.	4.22	Average, 4.21 per cent. N.
1000	42.18	4.22	
1000	42.02	4.20	

¹ Kubel-Tiemann, *Untersuchung von Wasser*, Braunschweig, 1874, 55; also Fres. Quant. Anal., Johnson and Allen, N. Y., 1883, 473.

Nitrogen in Plants. Determined by Soda-lime.

FIRST SERIES.

Vines, roots, etc. ¹ mgm.	N. found. mgm.	Per cent. N.	Vines, roots, etc. mgm.	N. found. mgm.	Per cent. N.
A { 1103 1000 1000	15.42 14.36 14.08	1.398 1.436 1.408	C { 1000 1000 1000	5.78 5.78 5.78	0.578 0.578 0.578
Average, 1.417 per ct.			Average, 0.578 per ct.		
Total vines, roots, etc. = 11.8 gram @ 1.417 per cent. = 167.21 mgm. N.			Total vines, roots, etc. = 18.8 gram @ 0.578 per cent. = 108.70 mgm. N.		
B { 1000 1000 1000	12.17 12.17 12.17	1.217 1.217 1.217	D { 1000 1000 1000	8.06 8.06 8.24	0.806 0.806 0.824
Average, 1.217 per ct.			Average 0.812 per ct.		
Total vines, roots, etc. = 11.0 gram @ 1.217 per cent. = 133.87 mgm. N.			Total vines, roots, etc. = 11.6 gram @ 0.812 per cent. = 94.19 mgm. N.		
E { 1000 mgm. 1000 1000			Average, 0.822 0.806 0.822		
8.22 mgm. 8.06 8.22			0.817 per cent.		
Total vines, roots, etc. = 10.1 gram @ 0.817 per cent. = 82.52 mgm. N.					

SECOND SERIES.

Wt. vines, roots, etc. mgm.	N. found. mgm.	Per cent. N.	Wt. vines, roots, etc. mgm.	N. found. mgm.	Per cent. N.
1 { 1000 1000	63.60 63.00	6.36 6.30	2 { 1000 1000	149.4 148.7	14.94 14.87
Average, 6.33 per ct.			Average, 14.91 per ct.		
Total vines, roots, etc. = 18.4 gram @ 6.33 per cent. = 116.45 mgm. N.			Total vines, roots, etc. = 12 gram @ 14.91 per cent. = 178.92 mgm. N.		
3 { 1000 1000	135.8 135.8	13.58 13.58	4 { 1000 1000	148.7 148.4	14.87 14.84
Average, 13.58 per ct.			Average, 14.86 per ct.		
Total vines, roots, etc. = 11.7 gram @ 13.58 per cent. = 158.90 mgm. N.			Total vines, roots, etc. = 13.5 gram @ 14.86 per cent. = 200.62 mgm. N.		
5 { 1000 1000	63.60 62.80	6.36 6.28	6 { 1000 1000	56.9 56.9	5.69 5.69
Average, 6.32 per ct.			Average, 5.69 per ct.		
Total vines, roots, etc. = 24.7 gram @ 6.32 per cent. = 156.10 mgm. N.			Total vines, roots, etc. = 26.3 gram @ 5.69 per cent. = 149.6 mgm. N.		
7 { 1000 1000	56.9 56.9	5.69 5.69	8 { 1000 1000	79.0 79.0	7.90 7.90
Average, 5.69 per ct.			Average, 7.90 per ct.		
Total vines, roots, etc. = 27.8 gram @ 5.69 per cent. = 158.1 mgm. N.			Total vines, roots, etc. = 25.0 gram @ 7.90 per cent. = 197.50 mgm. N.		
9 { 1000 1000	71.2 70.6	7.12 7.06	10 { 1000 1000	103.2 102.6	10.32 10.26
Average, 7.09 per ct.			Average, 10.29 per ct.		
Total vines, roots, etc. = 26.3 gram @ 7.09 per cent. = 186.5 mgm. N.			Total vines, roots, etc. = 27. gram @ 10.29 per cent. = 277.80 mgm. N.		
11 { 1000 1000	64.2 63.6	6.42 6.36	12 { 1000 1000	139.2 139.2	13.92 13.92
Average, 6.39 per ct.			Average, 13.92 per ct.		
Total vines, roots, etc. = 33.0 gram @ 6.39 per cent. = 210.9 mgm. N.			Total vines, roots, etc. = 18.7 gram @ 13.92 per cent. = 260.22 mgm. N.		

Nitrogen in Nutritive Solutions determined, like that in Residual Solutions, by Method of Schulze-Tiemann.

FIRST SERIES

Solution I.	Solution II.	N. found.
12 cc. + 12 cc.		18.45 mgm.
12 cc.		0.00831 mgm.
	12 cc., }	0.01009 " }
12 cc. + 12 cc.		18.43 "
12 cc. + 12 cc.		18.43 "
Average of 24 cc. of solutions (12 cc. each) I and II,		18.43 "

¹ The weights include that of sand which adhered to the roots in varying proportions, and which thus accounts for the wide variations in the percentages of nitrogen.

SECOND SERIES.

Solution NI.		Solution NIII.	
Solution.	N. found.	Solution.	N. found.
25 cc.	38.84 mgm.	25 cc.	29.81 mgm.
25 cc.	38.70 "	25 cc.	29.61 "
25 cc.	38.70 "	25 cc.	29.76 "
25 cc.	38.70 "	25 cc.	29.70 "
Average 1 cc. Solution = 1.5499 mgm. N.		Average 1 cc. Solution = 1.1833 mgm. N.	

Nitrogen in Residual Solutions at End of Experiments.

FIRST SERIES.

Solution.		Nitrogen found.		Solution.		Nitrogen found.	
A	$\frac{1}{2}$ of extract.		3.573 mgm.	C	$\frac{1}{2}$ of extract.		0.651 mgm.
	$\frac{1}{2}$ "		3.597		$\frac{1}{2}$ "		0.685
	Total.....	7.176			Total.....	1.336	
B	3-7 of extract.		3.217 mgm.	D	4-5 of extract.		2.580 mgm.
	4-7 "		4.744		Total (calculated)...	3.096	
	Total... ..	7.961					
		Solution.				Nitrogen found.	
E	$\frac{1}{2}$ extract.		28.542 mgm.		$\frac{1}{2}$ extract.		0.993 mgm.
	$\frac{1}{3}$ "		18.803		$\frac{1}{2}$ "		0.993
	$\frac{1}{6}$ "		9.474		$\frac{1}{2}$ "		0.993
	Total.....	56.819			Total.....	1.986	

SECOND SERIES.

Solution.		Nitrogen found.		Solution.		Nitrogen found.	
1	$\frac{1}{2}$ extract.		0.683 mgm.	2	$\frac{1}{2}$ extract.		0.993 mgm.
	$\frac{1}{2}$ "		0.683		$\frac{1}{2}$ "		0.993
	Total.....	1.366			Total.....	1.986	
3	$\frac{1}{4}$ extract.		0.939 mgm.	4	$\frac{1}{2}$ extract.		6.395 mgm.
	$\frac{1}{4}$ "		0.938		$\frac{1}{2}$ "		6.403
	Total (calculated)....	3.754			Total.....	12.798	
5..No nitrates in extract.				5	$\frac{1}{3}$ extract.		0.40 mgm.
					$\frac{1}{3}$ "		0.38
					Total (calculated).. <td>1.17</td> <td></td>	1.17	
7..No nitrates in extract.				8	$\frac{1}{4}$ extract.		3.16
					$\frac{1}{4}$ "		3.18
					Total (calculated).. <td>12.63</td> <td></td>	12.63	
9	$\frac{1}{2}$ extract.		0.719 mgm.	10	$\frac{1}{3}$ extract.		11.87 mgm.
	$\frac{1}{2}$ "		0.719		$\frac{1}{3}$ "		11.91
	Total	1.438			Total (calculated).. <td>35.68</td> <td></td>	35.68	
11	$\frac{1}{3}$ extract.		0.88 mgm.	12	$\frac{1}{3}$ extract.		14.88 mgm.
	$\frac{1}{3}$ "		0.92		$\frac{1}{3}$ "		14.91
	Total (calculated)....	2.70			Total (calculated).. <td>44.69</td> <td></td>	44.69	

I may also add that the residual solutions tested with Nessler's reagent were for ammonia, but revealed only traces.

To test the ease and completeness of removal of nitrates from sand by washing, as was done in separating the residual solution for determination of its nitrogen, the following trials were made with solutions which were put in sand and then washed with pure water. The smallness of the amount of water required for complete washing out of the nitrates, which has also been observed elsewhere, was here very noticeable.

Nitrogen in form of BaN_2O_6	Amount of sand, 500 gram.	NO in solution added to sand, 0.212 gram.	NO in extract from sand, 0.214 gram.
Solution I and II.	"	0.224	0.223
"	"	0.395	0.393
"	"	0.395	0.395
"	"	0.263	0.262
"	"	0.263	0.263

Contributions from the Chemical Bureau, U. S. Department of Agriculture.

III.¹—THE CHEMICAL COMPOSITION OF THE PRODUCTS OF ROLLER MILLING OF WHEAT.

BY CLIFFORD RICHARDSON.

The hard spring wheats, which have been mentioned in a previous paper as being rich in albuminoids, under the ordinary process of low milling furnish a dark colored flour of little value. To overcome this the roller mills have been introduced and the wheat is converted to flour by gradual reduction.

The number of products and by-products produced in roller mills is large, and the object of the investigation described in this paper was an examination and analysis of them all, for the purpose of ascertaining the composition of various portions of the grain and of the finished flours and other material derived therefrom.

The process, described very briefly, consists in preparing the wheat for the rolls, or breaks, as they are called, by the removal

¹ The articles beginning on pages 289 and 302 should have been numbered I and II in this series.

of foreign seed, dirt, chaff, and certain portions of the outer coatings of the grain with their adherent hairs; putting the cleaned grain through a series of rolls, after each of which all the reduced portion is removed and collected as chop, the coarse material being cleaned from all adherent matter and fed to the following roll until it comes from the last one as mere bran; purifying the various chops by appropriate machinery, which removes shorts, dusty particles, etc., and grades the coarser part, consisting of the interior or floury portion of the grain, into middlings of various sizes; purifications of these middlings from all foreign matter; reduction of the purified middlings between rolls or with stones, in the first manner flattening the germ so that it can be removed in the bolt; and mixing the graded flours for the market.

These are the chief points of the process. The re-purification of the middlings not reduced in the first operation of this character, and the collection of the lower grades of flour produced, incidental to the imperfections of the process, are additional details to be studied.

From this explanation the names of the products mentioned will be intelligible. For a complete understanding of the analyses, however, it will be necessary to consider the structure of the wheat grain and to know the portions of it which are represented in the different products. In my original report both these points have been explained at length. It will suffice here to say in regard to the first that the grain consists, essentially, of the floury portion, the endosperm, around which extends a continuation of the germ known as the embryous envelope. The germ itself is at one end of the grain and quite distinct from the endosperm. About all the previous parts extend the outer envelopes, consisting of five different layers, known as the cuticle, epicarp, endocarp, testa and tegmen. These, together with portions of the embryous envelope, make up the bran.

As has been said, the analyses will show that the composition of any product is dependent on the proportion of different parts of the grain found therein. In the following list there is given, therefore, the results of a physical examination of each one, and in it will be found the explanation of many of the results of the analyses.

PARTS OF THE WHEAT GRAIN IN DIFFERENT MILL PRODUCTS.

2001. *Wheat as it enters the mill.* The whole wheat grain mixed with cockle, oats, and other foreign seed, as it comes from the thrasher.

2002. *Wheat prepared for the rolls.* The foreign seeds have been removed with the exception of a few grains of cockle and oats. The cockle is therefore to be found in subsequent parts of the process. The hairs have been largely rubbed off, together with portions of the cuticle. Some hairs are, however, still left, and portions of the cuticle remain attached and semi-detached, especially toward the crease. The grain as a whole presents a changed and much cleaner appearance.

2003. *Cockle and screenings.* Among the foreign seeds there are found principally cockle and a species of polygonum and oats, together with broken pieces of wheat, dirt, chaff, etc.

2004. *Scourings removed by cleaners.* These consist almost entirely of cuticle and hairs, but portions of epicarp, with the hairs still adherent, and of endocarp are present. Treatment with iodine reveals a small amount of endosperm or starch, and shows the inner part of the outer coats of the grain is the most highly nitrogeous. The contrast between the embryous membrane and endocarp, and the epicarp and cuticle is prominent. The embryous membrane is recognized by its roundish cells; the endocarp by its transverse cells, twice as long as broad, and packed closely and regularly, like cigars, which has given it the name of cigar coat, and the epicarp by its very long and irregular cells arranged longitudinally, the cuticle being of a similar sort.

2005. *First break.* The grain is split along the crease normally into two halves, but also frequently into fours, or even more irregularly. The glistening, hard, floury endosperm makes its appearance for the first time. Comparatively little flour or dust is made.

2006. *Chop from first break.* This consists principally of endosperm, but small portions of bran¹ and germ are present in the former, including all the various outer coats.

2007. *Second break.* In this break the greater part of the endosperm is separated from the bran, and is seen as large well-shapen middlings, together, of course, with some small stuff and dust.

¹ Bran is used in this description as denoting and including any part of the coats of the grain.

2008. *Chop from second break.* This is chiefly endosperm, with somewhat less bran than the previous chop. Whole germs and parts are numerous. The endosperm is of all sizes, but the greater portion of large angular fragments. The bran includes portions of all the outer coverings, while dusty matter and starch grains are quite abundant.

2009. *Third break.* The endosperm is so completely separated in this break that it only remains in scattered patches upon the bran, and the embryous membrane is quite visible.

2010. *Chop from third break.* The middling or particles of endosperm are much finer, and there is more dust. Small portions of germ are plentiful. The branny particles are similar in nature to those in the last chop, but smaller, and there is more dust of a nitrogeneous kind.

2011. *Fourth break.* Only to be distinguished from No. 2009 by the slightly cleaner bran.

2012. *Chop from fourth break.* Not very different in appearance from 2010, except that it is composed of more finely divided particles.

2013. *Fifth break.* Still cleaner bran than 2011. It still holds a very appreciable portion of endosperm.

2014. *Chop from fifth break.* This chop contains a great deal of branny matter, including pieces of epicarp, endocarp, and embryous membrane. The endosperm is very fine and much mixed with germ. Of course, in all these products, portions of the testa and tegmen are present, but they are not easily seen except in careful preparations.

2015. *Sixth break.* Barely distinguishable from bran.

2016. *Chop from sixth break.* Very largely made up of small pieces of branny material and germs. The endosperm which is present is very fine.

2017. *Bran.* This is composed practically of epicarp, endocarp, and embryous membrane, the cells of the latter having been very little disturbed. There is still a little cuticle and endosperm left, but they have mostly disappeared in previous operations.

2018. *Shorts.* These are made up of all the different parts of the grain in rather a fine condition, some of the branny particles having endosperm still adherent to them.

2019. *Middlings, Uncleaned, No. 1.* These are the largest sized middlings, and consist in themselves of clean, angular fragments of

endosperm, but they are mixed with considerable shorts and many whole and broken germs. They are the most impure of the five, and an analysis will show this fact.

2020. *Middlings, Uncleaned, No. 2.* All the particles are finer than in the previous middlings, and less germ and bran is present, which will produce a corresponding change in their chemical composition.

2021. *Middlings, Uncleaned, No. 3.* Still finer than No. 2, and less bran and germ.

2022. *Middlings, Uncleaned, No. 4.* Finer than No. 3, and less bran and germ.

2023. *Middlings, Uncleaned, No. 5.* The finest of all the middlings, with almost no bran and germ. The effect of cleaning will be small.

2024. *Middlings, Cleaned, No. 1.* Many of the lighter particles of bran removed, but there is much remaining, as well as of the germ.

2025. *Middlings, Cleaned, No. 2.* The bran is to a large degree removed in cleaning these middlings, but the germ, of course, remains.

2026. *Middlings, Cleaned, No. 3.* The bran is almost all gone.

2027. *Middlings, Cleaned, No. 4.* These middlings are practically quite clean and pure endosperm. Only here or there a particle of bran or germ.

2028. *Middlings, Cleaned, No. 5.* Quite clean, and very small in size.

2029. *First middlings, reduction on smooth rolls.* The germ is flattened, and the endosperm reduced in size.

2030. *Chop from first reduction of middlings.* This sample appears to be misplaced, as it contains much bran and germ.

2031. *Second middlings, reduction on smooth rolls.* A sample of this reduction was not furnished.

2032. *Chop from second reduction of middlings.* This chop contains a few particles of bran and germ.

2033. *Third middlings, reduction on smooth rolls.* The germ is prominent in its flattened condition.

2034. *Chop from third reduction of middlings.* The bran and germ have been almost entirely removed.

2035. *Fourth middlings, reduction on smooth rolls.* Like the middlings themselves, merely reduced in size.

2036. *Chop from fourth reduction of middlings.* Here and there a small particle of bran seen.

2037. *Fifth middlings, reduction on smooth rolls.* Resembles of course the fifth middlings.

2038. *Chop from fifth reduction of middlings.* This is not as white as the chop from the fourth reduction, as it contains bran and germ in small quantities.

2039. *Flour from the first reduction.* The grains of endosperm are clean and sharp.

2040. *Flour from the second reduction.* The grains are not as sharp as those from the first reduction.

2041. *Flour from the third reduction.* Very much like the flour from the second reduction, but perhaps a little lumpier.

2042. *Flour from the fourth reduction.* More coherent and yellower than previous flours.

2043. *Flour from the fifth reduction.* There is no specimen of this flour.

2044. *Tailings from middlings purifier, No. 1.* These tailings are coarse. They contain much bran, mixed with germ, and a considerable amount of large middlings.

2045. *Tailings from middlings purifier Nos. 2, 3, and 4.* Much finer than the previous tailings and freer from germ and endosperm.

2046. *Tailings from middlings purifier No. 6.* Largely composed of fine endosperm, mixed with bran and germ.

2047. *Tailings from the first reduction.* These are made up of about equal parts of fine endosperm and of bran and germ.

2048. *Tailings from the second reduction.* These are finer than the first tailings, and contain more germ. There are also present pieces of endosperm, flattened like the germ.

2049. *Tailings from the third reduction.* Still finer, with much flattened endosperm, and less grain and bran.

2050. *Tailings from fourth reduction.* Very finely divided and flattened endosperm, with only about 10 per cent. of bran and germ. This should be very evident in the analysis.

2051. *Tailings from fifth reduction.* Coarser than the fourth tailings, and like the third in quality.

2052. *Re-purified middlings.* Coarse pieces of endosperm, with much bran and germ.

2056. *Bakers' flour.* Slightly yellow in color. The grains lack distinctness, making the flour lumpy.

2057. *Patent flour.* A clear, white grain.

2058. *Low grade flour.* The grain is soft and the flour dark and lumpy. Particles of bran and germ are prominent.

2059. *Break flour.* Physically like the bakers' grade in appearance, but particles of bran and germ are present, making it of less value.

2060. *Stone flour.* This flour is white, of a fair grain, with a very little bran.

2062. *Flour from first tailings.* A very good, free grain, but a little branny.

2063. *Flour from third tailings.* A free grain, but quite branny and yellow.

2064. *Flour from second tailings.* This flour resembles that from the first tailings, but contains more bran and is yellower.

2070. *First germ.* This is made up of the finest particles of germ and contains the largest proportion of middlings and bran.

2071. *Second germ.* The largest particles of germ, with little bran and endosperm.

2072. *Third germ.* A medium between the two former.

2074. *Bran-duster flour.* This is black in color and lumpy. It has little grain and a small portion of bran.

2077. *Stone stock, No. 2.* A good middling, with a little bran and germ.

2078. *Stone stock, No. 3.* This is not as good as No. 2, and holds more bran and germ.

2083. *Tailings from sixth break.* This is made up of about half badly shaped and flattened pieces of endosperm, the rest being bran, with a little germ.

2084. *Tailings from first centrifugal reel.* Largely flattened endosperm; the rest germ, with a little bran.

2085. *Tailings from second centrifugal reel.* These are largely bran and flattened endosperm, with a little germ.

2086. *Tail end of the tailings.* As would be expected, almost entirely bran, with a little adherent endosperm and a small amount of germ. The embryous membrane is still in place; in fact during the whole process there is very little of it removed from the bran, and were it the chief source of gluten there would be very little in any of the products. This, however, is not the case. It contains little or no gluten, being merely a continuation of the germ, and having a similar composition.

2087. *Dust from No. 1 middlings.* This is mostly cuticle epicarp and hairs, with smaller amounts of the more interior parts of the grain.

2088. *Dust from the dust-catcher.* This is all light, fluffy matter, and is made up of small particles from all parts of the grain.

A consideration of the preceding details furnishes us with the following information:

The preparation of the wheat for the rolls removes certain scorings, which consist of cuticle and bran, principally. They are richer in ash and oil than the whole grain and poorer in nitrogen, but, being very small in amount, probably not over one per cent. of the grain, as far as I am able to judge, they produce little effect on the relative composition.

The result of the first break is to show that the floury part of the grain, of which the chop from this break is largely composed, contains less fibre, ash, oil, and albuminoids than the whole wheat. In fact, the interior of the grain of which it is made up is the starchiest part.

So small a portion of the grain is removed in the first break that the feed of the second is about the same in composition as when it entered the first, and as close as the inevitable differences in selecting samples in a large mill will permit. In this break the greater part of the endosperm is separated from the bran.

It is, consequently, the starchiest and has the least ash, oil, fibre and albuminoids of any of the chops.

The feed for the third break, in a corresponding way, shows the effect of the removal of nearly all the endosperm, by largely increased percentages of the same constituents which are deficient in the chop of the previous break. The two analyses show that the bran contains much more nitrogen, ash, oil and fibre than the endosperm, but not, as it appears, necessarily more gluten.

As the wheat continues through the rolls the remaining endosperm is removed, but at the same time more particles of bran and germ get into the chop. The result upon the composition is shown by the rapid increase in the relative percentages of those constituents which have been mentioned as being more prominent in the bran.

The finished bran contains more ash, oil and fibre than any products, but not quite as much albuminoids, owing to the fact that the chop from the sixth break has a large portion of germ and embryous membrane, rich in nitrogen.

ANALYSES OF THE PRODUCTS OF ROLLER MILLING.

Serial Number.	Names.	Water.	Ash.	Oil.	Carbohydrates.	Fibre.	Albuminoids.	Nitrogen.	Phosphoric Acid.	Ratio nitrogen to phosphoric acid.	Gluten.	
											Moist.	Dry.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
C. A. PILLSBURY & CO., MINNEAPOLIS, MINN.												
2001	Wheat as it enters the mill.	9.66	1.91	2.61	69.94	1.70	14.18	2.27	.82	2.77
2002	Wheat prepared for the rolls.	9.07	1.79	2.74	70.37	1.68	14.35	2.30	.78	2.80	32.31	11.88
2003	Cockle and screenings.	9.03	2.05	4.32	66.12	4.23	13.65	2.18	.78	2.80
2004	Scourings removed by cleaners.	9.27	3.68	3.73	70.19	1.58	11.55	1.85	.76	2.43
2005	First break.	8.23	1.73	2.68	71.56	1.62	14.18	2.27	.91	2.49	31.92	11.69
2006	Chop from first break.	12.32	.88	2.68	70.44	1.13	12.95	2.07	.46	4.50	34.10	12.27
2007	Second break.	8.37	2.04	2.47	71.37	1.65	14.00	2.24	.98	32.78	32.78	11.80
2008	Chop from second break.	12.76	.57	1.68	71.82	.55	12.60	2.04	.34	5.94	36.88	12.56
2009	Third break.	9.92	2.55	5.25	65.10	2.13	15.05	2.41	1.33	1.81	32.09	12.04
2010	Chop from third break.	12.70	.78	1.86	71.10	.78	12.78	2.04	.42	4.86	37.19	13.00
2011	Fourth break.	8.18	3.30	4.09	66.20	3.00	15.23	2.44	1.44	1.07	27.88	10.54
2012	Chop from fourth break.	12.35	1.47	2.87	67.90	1.23	14.18	2.27	.75	5.05	30.52	11.64
2013	Fifth break.	7.62	5.16	4.91	61.76	4.80	15.75	2.52	2.58	1.08
2014	Chop from fifth break.	11.91	1.90	4.16	64.46	1.73	15.75	2.52	1.01	2.49	27.97	11.82
2015	Sixth break.	7.66	5.68	5.34	59.42	5.66	16.88	2.60	2.95	.81
2016	Chop from sixth break.	11.84	3.29	4.92	59.09	3.18	17.68	2.83	1.00	1.70	24.04	10.69
2017	Brans.	10.91	5.59	5.03	56.21	5.98	16.28	2.60	2.78	.94
2018	Shorts.	10.94	3.41	4.67	60.28	3.90	16.80	2.69	1.62	1.66
Middlings uncleaned —												
2019	No. 1.	12.71	1.27	2.73	68.78	1.03	13.48	2.16	.64	3.39	29.68	10.57
2020	No. 2.	12.18	1.04	2.16	70.49	.83	13.30	2.13	.54	3.94	32.99	11.49
2021	No. 3.	12.27	.70	1.80	71.52	.58	13.13	2.10	.36	5.83	35.52	12.21
2022	No. 4.	12.47	.68	1.75	70.69	.58	13.53	2.21	.40	5.82	45.82	15.69
2023	No. 5.	12.34	.61	1.75	70.24	.53	14.53	2.32	.33	7.53	43.82	14.86
Middlings cleaned —												
2024	No. 1.	12.67	1.07	2.12	70.16	.85	13.13	2.10	.59	3.56	34.03	11.16
2025	No. 2.	9.93	.65	1.90	74.09	.65	12.78	2.04	.33	6.18
2026	No. 3.	12.36	.59	1.70	71.67	.55	13.13	2.10	.24	8.75	44.43	14.99
2027	No. 4.	12.51	.52	1.77	71.57	.53	13.30	2.13	.29	7.34	51.93	17.85
2028	No. 5.	12.35	.51	1.62	70.74	.43	14.35	2.30	.23	10.00	46.15	14.87
Middlings, reduction on smooth rolls —												
2029	First middling.	12.64	.82	2.56	70.80	.58	12.60	2.02	.46	4.39	34.20	11.57
2030	Chop from first middling.	12.74	.72	1.99	71.72	.58	12.25	1.96	.40	4.90	32.16	10.91
2031	Second middling.
2032	Chop from second middling.	12.48	.57	1.68	71.24	.38	13.65	2.18	.34	6.41	41.36	13.65

Serial Number.	Names.	Water.	Ash.	Oil.	Carbohydrates.	Fibre.	Albuminoids.	Nitrogen.	Phosphoric Acid.	Ratio nitrogen to phosphoric acid.	Gluten.	
											Moist.	Dry.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
2033	Third middling	12.29	.61	1.86	71.91	.55	12.78	2.04	.34	6.00	36.70	11.81
2034	Chop from third middling	12.73	.79	2.01	71.29	.58	12.60	2.02	.43	4.79	34.58	11.68
2035	Fourth middling	11.43	.56	1.86	73.12	.43	12.60	2.02	.34	5.94	37.00	12.23
2036	Chop from fourth middling	11.72	.50	1.76	72.56	.33	13.13	2.10	.27	7.78	42.06	12.32
2037	Fifth middling	12.21	.65	2.68	71.85	.43	12.78	2.04	.40	5.10	36.25	11.97
2038	Chop from fifth middling	11.47	.56	2.03	72.06	.50	12.78	2.04	.37	5.57	40.84	13.11
	Flour from reduction of middlings —											
2039	First	12.03	.39	1.58	73.70	.25	12.05	1.93	.24	8.04	31.51	10.97
2040	Second	12.42	.44	1.66	72.55	.33	12.60	2.02	.24	8.42	37.04	12.07
2041	Third	11.54	.38	1.36	75.24	.28	11.20	1.79	.19	9.42	32.54	10.99
2042	Fourth	11.58	.40	1.42	72.92	.38	13.30	2.13	.20	10.65	37.90	12.52
2043	Fifth
	Tailings from middlings purifiers —											
2044	No. 1	12.33	3.30	4.96	60.06	3.25	16.10	2.55	1.61	1.60
2045	Nos. 2, 3 and 4	11.59	3.09	3.92	14.53	2.32	1.39	1.67	12.28	7.62
2046	No. 6	12.00	.90	2.37	69.10	1.10	14.53	2.32	.49	4.73	39.88	14.37
	Tailings from reduction —											
2047	First	11.78	3.26	5.03	60.32	2.63	16.98	2.72	1.82	1.47	13.04	5.47
2048	Second	10.35	3.38	4.37	59.87	2.08	19.95	3.19	1.68	1.90
2049	Third	11.72	2.35	4.37	63.27	1.66	16.63	2.66	1.34	1.98
2050	Fourth	12.09	.88	4.16	68.47	.40	14.00	2.24	.48	4.67	35.73	13.34
2051	Fifth	12.12	2.29	3.85	63.93	1.18	16.63	2.66	1.35	1.97	1.89	.67
2052	Repurified middlings	11.72	2.11	3.07	65.99	1.63	14.88	2.38	1.21	1.98	28.17	10.74
	Finished Flour —											
2056	Bakers'	12.18	.62	2.00	69.99	.33	14.88	2.38	.31	7.68	51.21	16.97
2057	Patent	11.48	.39	1.45	73.55	.18	12.95	2.07	.18	11.50	36.14	10.85
2058	Low grade	12.01	1.99	3.86	63.26	.93	17.95	2.74	1.16	2.36	10.01	4.26
2059	Break flour	12.48	.58	1.37	69.44	.23	15.40	2.46	.31	7.94	51.38	15.87
2060	Stone flour	12.04	.49	1.61	72.85	.23	12.78	2.04	.27	7.55	38.21	11.74
	Flour from tailings —											
2062	First	12.55	.62	2.93	70.25	.35	13.30	2.13	.39	7.10	39.13	12.85
2063	Third	12.50	.85	2.79	70.20	.58	13.13	2.10	.45	4.67	37.78	12.68
2065	Second	11.20	.76	2.03	72.28	.48	13.65	2.18	.30	5.59	43.25	13.87
2068	Cockle chop	12.45	2.79	4.34	64.01	3.63	12.78	2.04	.80	2.37
2069	Cockle bran	7.71	3.40	3.84	65.46	9.03	10.50	1.68	.83	2.02
2070	First germ	8.69	3.42	9.35	53.28	1.23	24.13	3.86	1.83	2.11
2071	Second germ	8.75	5.45	15.61	35.19	1.75	33.25	5.32	2.57	1.98
2072	Third germ	7.68	4.94	13.75	39.25	1.50	32.88	5.26	2.56	2.05
2074	Brander flour	11.78	1.17	2.70	70.20	.50	13.65	2.18	.66	3.30	58.59	13.72

Serial Number.	Names.	Water.	Ash.	Oil.	Carbohydrates.	Fiber.	Albuminoids.	Nitrogen.	Phosphoric Acid.	Ratio nitrogen to phosphoric acid.	Gluten.	
											Moist.	Dry.
		Percent.	Percent.	Percent.	Percent.	Percent.	Percent.	Percent.	Percent.	Percent.	Percent.	Percent.
2077	Stone stock —	12.15	.40	1.64	72.91	.25	13.65	2.18	.19	11.58	47.55	15.32
2078	No. 2.....	12.01	.55	2.12	71.76	.43	13.13	2.10	.28	7.50	46.39	15.15
2079	Tailings —											
2083	From sixth break.....	11.64	2.20	4.06	64.31	1.95	15.75	2.52	1.23	2.05	16.45	6.17
2084	From first centrifugal reel.....	11.42	2.15	3.44	66.56	1.20	15.23	2.44	.98	2.40	6.58	2.39
2085	From second centrifugal reel.....	11.07	2.85	4.73	61.82	2.20	17.33	2.79	1.47	1.88
2086	Tail end of the tailings.....	11.36	3.87	5.23	64.86	15.75	2.52	1.75	1.44	10.74	.41
2087	Dust from No. 1 middlings.....	11.03	1.83	2.73	68.86	5.20	14.35	2.30	.55	4.18	25.76	10.31
2088	Dust from dust catcher.....	11.53	1.17	2.64	69.01	1.65	14.00	2.24	.55	4.07	35.05	13.00
HARR & CUSSEL, GEORGETOWN, D. C.												
2089	Mixed wheat, clean.....	9.62	1.93	2.29	71.83	1.55	12.78	2.04	.98	2.08	30.00	11.03
2090	First break.....	8.13	2.03	2.46	72.30	1.60	13.48	2.16	1.05	2.05	29.17	10.42
2091	Second break.....	9.47	2.00	2.01	71.81	1.58	13.13	2.10	.91	2.30	34.02	11.87
2092	Third break.....	8.79	2.03	2.37	71.98	1.70	13.13	2.10	1.10	1.90	29.24	10.32
2093	Fourth break.....	8.91	2.39	70.97	1.75	13.05	2.18	1.14	1.91	34.08	12.23
2094	Fifth break.....	7.18	3.46	13.40	2.46	1.35	1.82	26.75	10.09
2095	Sixth break.....	9.38	4.76	16.10	2.58	2.46	1.04
2096	First middling.....	11.96	.49	1.22	75.30	.35	10.68	1.71	.25	6.84	32.09	9.92
2097	Second middling.....	11.89	.51	1.21	75.56	.33	10.50	1.68	.25	6.72	35.49	10.55
2098	Third middling.....	10.88	.50	1.19	75.45	.25	11.73	1.88	.24	7.83	42.10	13.32
2099	First middling through smooth rolls.....	9.87	1.84	2.00	71.08	1.18	13.13	2.10	.87	2.42	28.07	10.59
2100	Patent flour.....	12.98	.32	.92	75.60	.20	9.98	1.60	.16	10.00	29.55	9.08
2101	Bakers' flour.....	13.29	.47	1.26	72.45	1.50	11.03	1.76	.28	6.28	35.04	11.30
2102	Low-grade flour.....	12.59	1.05	2.33	69.10	.75	14.18	2.27	.58	3.91	35.96	12.81
2103	Germ middlings.....	11.10	2.41	3.74	66.59	1.63	14.53	2.32	1.19	1.94
2104	Feed middlings or tailings.....	8.53	3.75	4.96	62.21	4.10	16.45	2.63	1.98	1.32
2105	Bran middlings.....	8.24	6.39	5.52	56.77	6.13	16.45	2.63	.98	2.68
WARDER & BARNETT, SPRINGFIELD, OHIO.												
1855	Wheat.....	9.05	2.66	2.46	71.67	2.33	12.43	1.99	1.03	1.93	20.93	10.34
1856	Patent flour.....	12.32	.34	1.05	75.28	.33	10.68	1.71	.19	9.00	35.52	10.76
1857	Bakers' flour.....	11.98	.60	1.77	71.52	1.00	13.13	2.10	.33	6.56	38.29	12.30
1858	Low-grade flour.....	12.36	.69	1.00	75.04	.93	9.98	1.60	.30	5.33	28.37	9.96
1859	Middlings.....	8.49	4.28	5.94	60.64	3.15	17.50	2.80	1.12	2.50
1860	Bran.....	7.74	6.99	4.99	15.40	2.46	1.04
2190	Patent flour, second sample.....	13.59	.36	1.08	73.94	.35	10.68	1.71

The shorts are poorer in ash than the bran, also in oil and fibre, and this arises, probably, from the origin of the shorts in the more exterior coats of the grain.

The five classes of middlings, graded by sizes, present a regular decrease in ash, oil, and fibre, from the largest to the lowest. The albuminoids do not vary so much in amount, but, as will be seen later, they vary very much in quality. After cleaning, the analyses show what would be expected from the removal of branny particles and germ; but the same general relations are preserved.

The reduction of the middlings, of course, affects their composition but slightly; the tailings, although rich in nitrogen, being small in amount. They, like the tailings from the middlings purifiers, consist largely of bran and germ, mixed with some endosperm, and are therefore, with one exception, in which the tailings are made up of flattened endosperm, rich in ash, oil and albuminoids.

The different grades of flour vary somewhat, but within narrower limits than one would be led to expect from the composition of the middlings. Among the finished flours as graded for market, large differences appear, both in the physical properties and chemical composition. From a cursory glance it might be said that the low grade flour was the best, as it contains the most albuminoids, but its weakness lies in the fact that it has only 4 per cent. of gluten. The bakers' flour contains more ash, oil, fibre and albuminoids, and even more gluten than the patent, but owing to the increased amount of the three first named constituents it is proportionately lacking in whiteness and lightness. The patent flour certainly has the greatest number of desirable qualities.

Several other grades of flour, break flour, stone flour, and flours from the first, second and third tailings, are very similar, and, as far as the analyses go, good. The preliminary examination has, however, shown certain defects in each. The break flour is richer in albuminoids and gluten than any other, and if it were pure and its physical condition good it would be of value.

This process of reducing the middlings to flour is distinguished by the completeness with which the germ is removed by flattening it between rolls and separating it in the bolts. This furnishes three by-products which are known as first, second and third germ. They consist of the germ of the wheat mixed with a certain portion of branny and starchy matter, the second germ being more nearly

pure. They all contain much ash, oil and nitrogeous substance, and, if left in the flour, blacken it from the oxidation of the oil and render it liable to fermentation, owing to peculiar nitrogeous bodies which they contain. A proximate analysis appears in my original report.

The flour from the bran-dusters is much like that from the tailings, and like that from the stone stock, from a chemical point of view. This merely shows that chemical evidence alone cannot be depended on; for the bran-duster flour is a dirty, lumpy by-product, while the stone stocks are valuable middlings.

Analyses of the dust from middlings and from the dust-catcher are remarkable, for they both show the presence of much gluten, and of much fibre in the first. This is due to their both containing both bran and endosperm.

To follow the gluten through the different products it is necessary to go back to the breaks. The amount in the various chops does not vary greatly. There is an apparent anomaly in the fifth and sixth breaks, however, where no gluten is found in the feed, but much in the chop. This is owing to the fact that the feed has become so branny at this point that by the usual method of washing to obtain the gluten none is recovered. After it is loosened from the bran in passing through the rolls it is readily collected.

Among the middlings, both cleaned and uncleaned, the fourth is the richest in gluten, and the result of the process of cleaning is to increase the amount, although slightly diminishing the nitrogen, which is due to the removal of the branny matter, which, though rich in nitrogen, is poor in gluten.

In the products of the reductions on smooth rolls the chops from the higher middlings are the richest, and if the analyses of the flours were complete, No. 4 would probably contain more than the lower numbers.

The tailings are remarkable, as has been already said, not so much that No. 1 has no gluten, but that Nos. 2, 3, 4 have 7.62 per cent. and No. 6 as much as 14.37 per cent. The regular increase shows that in the highest numbers it is due to the large portion of endosperm which they were found to contain. No. 1 consists almost entirely of the outer coatings of the grain; Nos. 2, 3, 4, of the same, mixed with a large portion of endosperm, in an attached condition, while in No. 6 it is as difficult to discover anything but

floury material. The small percentage of ash also shows that it can contain but little bran.

In the same way No. 4 tailings, from the reductions, has 13.34 per cent. of gluten, due to the large amount of endosperm which it contains, and in this case, too, the fact is presaged by the low percentage of ash. The remaining tailings of this class have little or no gluten, with the exception of No. 1, as they contain very little endosperm.

The results, as a whole, warrant the conclusion that less gluten is wasted in the by-products than would be imagined. A knowledge of the percentage of each product made is necessary for a complete understanding of this relation.

The analyses of the products of milling Virginia and Ohio wheats by the roller process are not as complete as those of the Minnesota grain. They show variations in the different products, not, however, exactly corresponding ones. Among the flours, for instance, the low grade Virginia, instead of containing less, has more gluten than the bakers' grade. This is probably due to the greater softness of the Eastern wheat, in consequence of which it is less suited to the process. Among the Ohio flours, although the low grade does not exceed the other brands in the amount of gluten which it contains, it approaches closely to them, and it is reasonable to conclude that the hard spring wheats are more suited to the process than the softer winter varieties.

It has been impossible to complete analyses of all the ashes of the different products which have just been described, but that of the ash of the patent flour shows a marked decrease over that of the original grain in the percentage of magnesia which it contains, made up by a corresponding increase in lime. The phosphoric acid, too, is higher, and determinations of this constituent show that the relation between it and the nitrogen is an intimate one.

Starting with a ratio of 2.8 in the whole grain, with every purification the figure rises until it reaches the highest grade middlings and patent flour; that is to say, as we approach the more perfectly purified products there is a greater loss of phosphates than of nitrogen. The highest ratios are found in the patent flours and the chop and middlings which lead to this product. In the flours from the reduction of different grades of middlings the change in the ratio is gradual, and corresponds

closely to the inverse change in the amount of phosphates in the ash. A high ratio denotes, therefore, a deficiency in phosphates, and this is the chief fault with our high grade flours.

For more complete details in regard to this subject, reference must be made to Bulletin No. 4 of the Bureau of Chemistry, United States Department of Agriculture.

WASHINGTON, Nov. 1884.

IV.—THE TIME ELEMENT IN GLUTEN DETERMINATIONS.

BY WM. FREAR.

Few writers on food or plant analysis, in describing Beccari's method for the determination of gluten in grain or flour, make note of the influence of the length of time which elapses between the preparation of the dough and the separation of the starch, upon the quantity of gluten obtained. It has, however, long since been observed by some of the chemists who have given particular attention to the analysis of cereals and albuminoids, that better results are obtained if the dough is allowed to stand for some time before washing: Von Bibra¹ recommends a period of fifteen minutes; Ritthausen² makes it thirty minutes; Peligot³ says that from thirty to fifty minutes is best. Still, though these authors mention definite periods, their disagreement and the fact that in no case are there given experimental data leading to the adoption of the limits named, indicate that they have been arbitrarily selected.

The experiments of Weyl and others having pointed to the conclusion that gluten is produced by the action of an unorganised ferment, MM. Benard and Girardin⁴ made some experiments to determine the rapidity and duration of its action. Three equal portions of dough from the same flour were washed, one immediately after preparation, another thirty minutes after, and the third three hours after. The percentages of "moist gluten" obtained from experiments on three samples were as follows:

Immediately.	30 minutes.	3 hours.
24.40	27.40	30.80
26.20	29.20	31.20
22.00	28.20	28.40

¹ Die Getreidearten und das Brod, 1861, p. 140.

² Die Eiweisskörper der Getreidearten, Hülsenfrüchte und Oelsamen, 1872, p. 3.

³ Traité de Chimie Analytique appliquée à l'Agriculture, Paris, 1883, p. 371.

⁴ J. Phar. et Chim. (5) 4, 1881, p. 127-128.

The third sample contained more moisture than the others.

From these results the authors conclude that it is best to wait at least *three hours* before washing.

Recently, in the course of a number of gluten determinations, I was led, without any knowledge of the investigations of MM. Benard and Girardin, to experiment upon the same point. A few trials having shown the great increase during the first thirty minutes, the samples of dough were allowed to stand for longer periods, in order to fix the point at which the formation of gluten was practically complete. In preparing the dough 20 grams of the sample were mixed with 10-15 cc. of water. The results stated in the percentages of "dry gluten" obtained, were as follows:

H. min.	Per cent.	H. min.	Per cent.	Difference.
.45	10.94	2.35	10.76	— .18
.55	11.81	2.35	11.58	— .23
1.00	10.77	3.00	10.75	— .02
1.00	11.01	2.00	11.00	— .01
1.15	11.22	3.40	11.21	— .01
2.15	12.41	3.00	12.77	+ .36
1.30	10.55	2.30	9.95	— .60

The last column is surprising because, instead of showing an increase during the longer interval, it seems to indicate an almost invariable decrease. This, however, is explained by the fact that on standing the dough is covered by a pellicle which gradually becomes harder and thicker, and on washing, instead of becoming homogeneous, breaks into small pieces, which will, unless great care be exercised, wash out with the starch, carrying incorporated with them a very considerable portion of the gluten. Thus, No. 7 being an unbolted flour, the loss was much greater because bran renders the pellicle more difficult to soften. In No. 6, the difference in time being small, the increase is more probably due to an accidentally greater loss in the first of the duplicates.

These results, then, indicate that the formation of gluten is practically complete in from forty-five minutes to an hour after the dough is prepared; and that the adoption of a longer period, by increasing the difficulty of the following parts of the process, introduces a source of error rather than a condition favorable to the fairest results.

Contributions from the Chemical Laboratory of Harvard College.

XLV.—ON THE REDUCTION OF CAMPHOR TO BORNEOL.¹

BY C. LORING JACKSON.

In 1883, Menke and I published a paper² entitled "A New Method of Preparing Borneol from Camphor," in which we described, first, the complete reduction of camphor to borneol by sodium and moist toluol; secondly, a convenient practical method for making borneol by the action of one and a third times the theoretical amount of sodium on an alcoholic solution of camphor, and purifying the product by crystallisation from hot alcohol; and thirdly, explained the formation of the borneol by the following reaction:



In the first number of the *Monatshefte für Chemie*³ for this year, Kachler and Spitzer published an examination of our method, which led them to the conclusion that it was worthless, since in three experiments they obtained products, the larger part of which melted from 179° to 181°, and in no case higher than 185° even after fractional crystallisation and sublimation (borneol melts at 199½°); while another set of experiments showed that as much as 82.8 per cent. of the hydrogen evolved by the sodium in one case, and 54.1 per cent. in another, escaped in the free state. They also determined how much borneol had been formed in one of their experiments by converting the crude product into chlorides, and determining the chlorine, which showed 22.8 per cent. of borneol to 77.2 per cent. of unaltered camphor; and, therefore, doubt whether the formation of borneol was due to reduction by nascent hydrogen at all, but ascribe it rather to the action of the sodium itself, as if in the presence of an indifferent liquid (Baubigny's reaction).

It is to be remarked, however, that they have confined their attention to the reduction of camphor by sodium and alcohol, and were not justified in thus rejecting our reaction,



¹ From the Proceedings of the American Academy, communicated by the author.

² This Journal **5**, 270.

³ *Monatshefte für Chemie* **5**, 50.

as they had not repeated the experiment described in the beginning of our paper, in which 25 grams of camphor by the action of an excess of sodium and moist toluol were completely converted into borneol, as shown by the melting-point $197-198^{\circ}$, and a combustion. That this observation, and therefore the reaction given above, are correct, has been proved by Immendorff under the direction of Anschütz, who has published a most welcome paper¹ on the subject in the interval between the appearance of Kachler and Spitzer's paper and this answer, which has been much delayed, because, since the publication of their paper, I have had no laboratory at my disposal until this autumn. Immendorff's proof consisted in increasing the amount of sodium used upon the alcoholic solution of camphor from $1\frac{1}{2}$ to $3\frac{1}{2}$ times the theoretical amount, when he obtained a product which, after crystallisation from petroleum ether or sublimation, melted at $199-200^{\circ}$, and was proved to be pure borneol by analyses of its chloride. Although in this way he confirms our theoretical views, he did not obtain better results from our practical process than Kachler and Spitzer, as he got as low a melting-point (181°) as they, when he used the amount of sodium recommended by us ($1\frac{1}{2}$ times the theory), and even with twice the theoretical amount did not get a melting-point above 188° . As we had got a melting-point of 193° for the crude product, I felt that it was advisable to take up the subject again, and study the conditions of the reaction more carefully, especially as both Kachler and Spitzer, and Immendorff, dwell on the interest of this process from a theoretical as well as a practical point of view.

The result of my experiments is, however, that, even when in following our original directions I tried to make the conditions as unfavorable as possible, the melting-point of the crude product was $187-188^{\circ}$, and in other repetitions 188° and 189° , so that my products with one and a third times the theory of sodium melted 6° to 8° higher than the corresponding ones of Immendorff, and as high as his with twice the theory,² but not so high as our previous melting-point of 193° . Although, as I could not get such low melting-points as the foreign chemists, I have been unable to find the cause of the difference between their results and ours, I have succeeded in modifying the process for making borneol, so as to make it superior even to the much improved form given to it by Immendorff; for I soon found that a better result was

¹ Ber. d. ch. G. **17**, 1036.

² With twice the theory I obtained melting-point 194° .

obtained if less alcohol was used, and upon reducing the quantity by one-half, that is, using five times the weight of the camphor, instead of ten times, as we advised originally, I obtained with one and a third times the theory of sodium a product¹ melting at 193° without purification, while increasing the sodium to twice the theory gave me the same result as Immendorff's with the larger quantity of alcohol, and three and a third times the theory, that is, a crude product having the melting-point 196° , which was not raised by the use of more sodium, and gave by one crystallisation from ligroine² 52 per cent., and in a second case 45 per cent. of pure borneol, melting between 199° and 200° . This same melting-point was obtained in four different experiments; and that the yield was not better from Immendorff's method was proved by following his directions carefully in another experiment, the product of which gave, after treatment with ligroine, not more than 50 per cent. of pure borneol. I should judge, too, from the results of my experiments, that cooling and stirring the liquid had a favorable action on the process, but their effect is comparatively small.

The work described above has led me to the following method for the preparation of borneol from camphor, which becomes in this way one of the simplest and easiest operations in organic chemistry: 10 grams of camphor are dissolved in 50 grams of common alcohol in a small beaker, and treated with 6 grams of sodium added in pieces of from 0.1 to 0.2 gram. At first, only two pieces are added at a time, the addition of fresh sodium taking place only after what has been already put in has disappeared; but after the fourth gram, a gram may be added at once, cut in pieces of the size mentioned above. The object should be to keep up a gentle effervescence, and it is well to stir the liquid frequently, to keep it cool by immersing the beaker in a dish of water, and toward the end of the process, when the action has become sluggish, to add from time to time a few drops of water to prevent the liquid from becoming pasty. After all the sodium has been used up the crude borneol is precipitated by water, washed till free from alkali, dried by pressure between cloth or filter-paper, and purified by crystallisation from ligroine.

¹As this substance is identical with the crude product described in my paper with Menke, I am inclined to think that we must have used less alcohol than the amount recommended by us in that paper.

²The crystallisation from ligroine, as recommended by Immendorff, is far superior to the crystallisation from hot alcohol, used by Menke and me.

Finally, I would add that sodium amalgam reduces an alcoholic solution of camphor, although the action is so slow that it is of no value as a practical method, the melting-point being raised only to 183° by action during two weeks, part of the time on the water-bath. The fact, however, deserves mention, because in Beilstein's Handbuch, p. 1763, it is stated that sodium amalgam does not act on camphor.

THE ACTION OF LIGHT ON SILVER CHLORIDE.

BY SPENCER B. NEWBURY.

The blackening of silver chloride when exposed to light has been explained in various ways, but the conclusions of even the most careful observers show no agreement, and but little accurate experimental work seems to have been done to clear up the problem. Von Bibra (Journ. f. Prac. Chem., 1875, p. 39) has carefully collected the results of all important observations in this field, and in the same paper gives an outline of his own work on silver chloride and the *subchloride* produced by heating silver citrate in a current of hydrogen and treating the product with hydrochloric acid. The authorities quoted in this paper agree upon the following facts:

1. In the darkening of moist silver chloride by the action of light, chlorine is liberated, apparent by its odor, and easily recognisable by the usual tests.
2. The darkening effect is retarded by the presence of free chlorine, ferric and cupric chlorides, and nitric acid, and accelerated by stannous chloride.
3. Blackened silver chloride is not decomposed by nitric acid; when treated with ammoniac hydrate, silver chloride is dissolved, and a residue of metallic silver is left.

In addition, Von Bibra's investigations led him to the following conclusions:

1. Dry silver chloride, exposed to light, with frequent stirring until completely blackened, shows no perceptible loss of weight. The blackened chloride is not decomposed by nitric acid.

2. Silver citrate heated to 100° in a current of dry hydrogen until constant weight is obtained, yields a black powder which is soluble in a very large quantity of cold water, giving a red solution, and which, on treatment with hydrochloric acid, yields pure silver subchloride, the formula of which is Ag_4Cl_3 . This compound is decomposed by nitric acid, leaving silver chloride; also by ammonia, leaving metallic silver. Von Bibra concludes that since chloride of silver, blackened by light, is not affected by nitric acid, it cannot be silver subchloride.

As there are on record no accurate observations of a loss of weight on exposing silver chloride to light, I first made this point the subject of a series of experiments. The calculated quantity of silver nitrate necessary to yield .1000 gram of chloride was accurately weighed out, dissolved in 100 cc. of water contained in a flask, and precipitated by the addition of a very minute excess of sodium chloride dissolved in the same quantity of water. The finely divided precipitate remained suspended in the water for a considerable time, subsiding after several hours' exposure to light. The exposed substance was in every case brought upon a weighed Gooch filter (consisting of a platinum crucible, the bottom of which is perforated and covered with a thin layer of asbestos), dried at about 140° , and weighed. By the use of this admirable contrivance it was found possible to reduce to a minimum the experimental errors which have hitherto made observations on this point unsatisfactory.

To ascertain the amount of possible loss, the precipitate produced in the flask was several times directly weighed without exposure to light, with the following results:

	Found.	Calculated.
1.	.0996	.1000
2.	.0997	"
3.	.0997	"

A number of flasks were prepared as described, and exposed for varying periods to direct sunlight; meanwhile a current of air was continuously drawn through the liquid to retard subsidence and carry off liberated chlorine. After the exposure the precipitate was brought on to the filter, dried at 140° , and weighed; then treated on the filter with hot ammonia solution, and finally the filter with the residue of metallic silver dried and weighed again. In every case a distinct loss of weight was observed, and

the residue of metallic silver after treatment with ammonia generally corresponded approximately to the loss of chlorine.

Since the precipitate of silver chloride soon collects at the bottom of the flask as a black, curdy mass, it is evident that but little additional effect will be produced by light after the subsidence is complete.

Four similar flasks, as described above, exposed side by side to direct sunlight for several days, gave the following results:

	Weight.	Loss.	Metallic silver.	Met. silver calculated from loss.
1.	.0967	.0029	.0054	.0085
2.	.0979	.0018	.0076	.0054
3.	.0969	.0027	.0078	.0081
4.	.0982	.0015	.0062	.0045

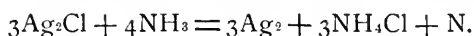
I am not prepared to offer any explanation of the discrepancies between the amounts of metallic silver found and those calculated from the loss of chlorine. In a very large number of experiments the same lack of agreement showed itself. The figures given serve, however, to prove that there is a distinct and weighable loss of chlorine on exposing silver chloride to light.

Similar experiments were made with the addition of small quantities of stannous chloride. In this case the precipitate is quickly blackened on exposure, soon assuming a gray color, and does not completely subside even after standing some days. On examination the precipitate was found to consist almost wholly of finely divided metallic silver.

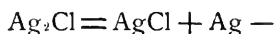
In order to ascertain, if possible, whether a *subchloride* results from the action of light on silver chloride, or whether metallic silver only is formed, 10 grams of silver chloride were exposed to the sun under water for several days. During the exposure the substance was frequently stirred to present fresh surfaces to the light, and a current of air was constantly drawn through the liquid, as in former experiments. A small quantity of the resulting dark purple substance, dissolved in ammoniac hydrate, left a residue of silver equal to 2.94 per cent. of the amount treated, which gives by calculation a loss of chlorine of .96 per cent. I now hoped to isolate the product of reduction by dissolving out the undecomposed chloride, exactly as in the *fixing* of a photograph. The reagents employed for this purpose were sodium thiosulphate, potassium cyanide, and sodium chloride. In each case, *metallic silver only*

resulted. Even a cold concentrated solution of sodium chloride, frequently renewed, dissolves finally the last trace of silver chloride, and leaves a residue of gray, finely divided metallic silver. The purity of this residue was proved by a number of careful quantitative determinations.

These results certainly lead to the conclusion, that in the blackening of silver chloride by light, metallic silver is formed, and not a subchloride. Otherwise we must assume that the subchloride is decomposed into silver and silver chloride by the action of a cold solution of sodium chloride: which is at least highly improbable. The same conclusion has been reached by other investigators, but the experimental proof given by the action of solvents has been, as far as I know, heretofore lacking. Mr. P. C. Duchochois, whose work is reported in Anthony's Photographic Bulletin for June and November, 1884, concluded that no subchloride is formed, from the fact that after dissolving blackened silver chloride in ammonia, no ammonium chloride is to be found in the solution; supposing the reaction to be as follows:



There can, however, be no objection to writing the reaction thus:



in which case the ammonium hydrate simply plays the part of a solvent of silver chloride; hence it does not seem to me that the action of ammonia throws any light on the constitution of the substance.

The only remaining evidence of the existence of silver subchloride is the fact that the blackened compound is not dissolved by nitric acid. This fact Von Bibra cites as evidence that the substance is *not* subchloride, since his subchloride prepared from reduced silver citrate *is* decomposed by nitric acid. It has been suggested that the silver may be present in a passive form, but it seems to me more probable that the action of the acid is merely retarded by the presence of a large amount of insoluble chloride. Moreover, I find that long boiling with dilute acid does dissolve some of the silver. A sample of blackened silver chloride which gave on treatment with ammonia 2.94 per cent. silver, showed after boiling three times with fresh additions of dilute nitric acid, 2.74 per cent., 2.26 per cent. and 1.98 per cent. respectively.

I have made many experiments with a view to prepare silver subchloride from the citrate exactly as Von Bibra describes, but although great precautions were taken to thoroughly dry and purify the hydrogen and the silver citrate used, I have never succeeded in obtaining a constant weight. In every case, however, the chloride prepared by acting on the reduced citrate with hydrochloric acid, yielded only metallic silver on treatment with sodium chloride solution. Although I do not regard these last experiments as conclusive, and am at present engaged in repeating and extending them, they are sufficient to strengthen the doubt which many chemists have expressed, as to the existence of the subsalts of silver.

LABORATORY OF CORNELL UNIVERSITY, Jan. 10, 1885.

MINERALOGICAL NOTES.

BY EDGAR F. SMITH.

I. PECTOLITE.

This mineral occurs in Lehigh County, Pa., upon limestone and intimately associated with stilbite. Its exact locality is Hosensack Station, on the Perkiomen Railroad. It usually consists of compact masses of acicular crystals, of a grayish color. When reduced to powder the material is woolly and adheres to the pestle. The specific gravity is 2.6. Several analyses were made by Mr. E. B. Knerr and myself, with the following result:

SiO ₂	55.17 per cent.
Fe ₂ O ₃	.80
CaO	30.00
K ₂ O	.37
Na ₂ O	9.02
H ₂ O	4.63
	<hr/>
	99.99

From what information we have obtained, it would seem that this is the first time that petcolite has been observed in the State.

2. TITANITE.

This mineral, rather rare in Pennsylvania, we have also found in Lehigh County, Lower Milford Township, about two miles distant from Hosensack Station. It occurs in the same region in which we observed an olive-colored garnet, previously described in this Journal, Vol. 5, No. 4. The titanite crystals are well defined, but not more than half an inch in length. They are associated with green pyroxene crystals. Their color is a dark brown. Specific gravity 3.45. The analysis of the above made by Mr. Knerr and myself gave :

SiO ₂	34.87 per cent.
TiO ₂	43.41
CaO	21.75
	<hr/>
	100.03

Minerals, from new localities, have been examined in this laboratory as follows :

3. GLAUCONITE, APOPHYLLITE, HEULANDITE.

By E. B. Knerr and J. Schoenfeld.

The glauconite is from the falls of French Creek, Chester County, Pa., where it occurs in cavities of a feldspar. It has very much the appearance of earthy chlorite. Specific gravity 2.2. The analysis showed :

H ₂ O	8.43 per cent.
SiO ₂	52.86
Al ₂ O ₃	7.08
Fe ₂ O ₃	7.20
FeO	19.48
MgO	2.90
CaO	trace
K ₂ O	2.23
Na ₂ O	trace
	<hr/>
	100.18

The apophyllite is also found in the same locality. It occurs among the rocks met with in the mining of iron ore. The specimen examined was composed of rather large, well defined forms, having largely developed prism faces. Specific gravity 2.30. The analysis of the above yielded :

H ₂ O	16.80 per cent.
SiO ₂	51.88
CaO	25.31
K ₂ O	6.30
Fl	...
<hr/>	
	100.29

The heulandite is from Adamstown, Lancaster County, Pa. The crystals, although small, show the following faces, ∞P , $(\infty P \infty)$, oP , $-P$, $-2P \infty$, $(2P \infty)$, $(P \infty)$. They are found in cavities and between layers of trap rock. The associated minerals are quartz, calcite, hornblende, and several others, probably zeolites, which could not be examined from lack of sufficient material. Specific gravity 2.2. The analysis showed :

H ₂ O	16.61 per cent.
SiO ₂	57.68
Al ₂ O ₃	17.05
CaO	6.78
MgO	.69
K ₂ O	1.13
Na ₂ O	trace
<hr/>	
	99.94

4. MENACCANITE.

By E. B. Knerr and D. B. Brunner.

This mineral occurs in rather large and good crystals in quartz, near Adamstown, Lancaster County, Pa. Specific gravity 4.6. By analysis we obtained :

	I.	II.	III.
SiO ₂	.50 per cent.	.82 per cent.	.90 per cent.
TiO ₂	13.31	12.84	13.31
Fe ₂ O ₃	53.36		
FeO	32.38		
<hr/>			
	99.55		

5. STILBITE.

By F. P. Davidson.

The specimen analysed was found at Rautenbush, Berks County, Pa. This locality has been already announced,¹ but as no analysis of the mineral is recorded, we give the following :

H ₂ O	18.46	18.60
SiO ₂	58.01	58.15
Al ₂ O ₃	13.75	12.47
CaO	7.76	} 9.82
MgO	1.38	
K ₂ O	.42	.43
Na ₂ O	trace	trace
	<hr/> 99.78	<hr/> 99.47

The usual forms of stilbite were present on the above specimen, the crystals being collected in radiating masses.

6. STILBITE.

By W. S. Hoskinson and D. B. Brunner.

Found at Fegley's Mine, Berks County, Pa., where it occurs upon granite associated with micaceous magnetite. Its usual appearance is in masses of radiating needles of white color. Specific gravity 2.2. Analysed, it shows the following composition :

H ₂ O	18.97 per cent.
SiO ₂	57.54
Al ₂ O ₃	12.67
CaO	7.85
MgO	1.72
K ₂ O	1.09
Na ₂ O	trace
	<hr/> 99.84

WITTENEERG COLLEGE, O., December 27, 1884.

¹ Genth's Mineralogy of Pa.

REMARKS ON SCHULZE'S PROCESS FOR THE QUANTITATIVE DETERMINATION OF THE HALOGENS IN AROMATIC COMPOUNDS.

BY L. P. KINNICUTT AND R. C. SWEETSER.

K. E. Schulze has recently described a method for determining the amount of chlorine, bromine or iodine in aromatic compounds, where the halogen is united to the carbon atoms of the side chains.¹

According to this method, an excess of a hot saturated alcoholic solution of argentic nitrate is added to a weighed amount of the compound, the solution boiled for five minutes, and the precipitate collected on a Gooch crucible.

Schulze, for lack of time and material, seems to have tried his method of analysis on only four substances, benzol chloride, benzoyl chloride, and the β -naphthoyl chloride and bromide. Further experiments with the process seemed desirable, and we have on this account analysed a number of the bromine derivatives of phenylpropionic acid, following as closely as possible the method as described by Schulze.

The α -phenylmonobrompropionic acid, $C_6H_5CH_2CHBrCOOH$.

Wt. taken.	Time of boiling.	Br found.	Theory.
0.3191 gram	20 minutes	34.44 per cent.	34.93

The next substance analysed, the phenyldibrompropionic acid, gave only one-half the theoretical amount of bromine; monobromstyrol being formed, which resisted further decomposition.

The phenyldibrompropionic acid ethyl ether, $C_6H_5CHBrCHBrCOOC_2H_5$.

Wt. taken.	Time of boiling.	Br found.	Theory.
0.3087 gram	5 minutes	23.43 per cent.	47.62
0.2860	10	23.74	...
0.2614	20	24.24	...

The α -phenyltribrompropionic acid, $C_6H_5CHBrCBr_2COOH$.

Wt. taken.	Time of boiling.	Br found.	Theory.
0.3191 gram	20 minutes	37.73 per cent.	62.54

¹ Berichte d. deutsch. chem. Gesell. **17**, 1675 American Chem. Journal **6**, 351.

The β -phenyltribromopropionic acid, $C_6H_5CBr_2CHBrCOOH$.

Wt. taken.	Time of boiling.	Br found.	Theory.
0.2950 gram	20 minutes	34.27 per cent.	62.54

The α -monobromocinnamic acid, $C_6H_5CHCBrCOOH$.

Wt. taken.	Time of boiling.
0.2885	20 minutes.

No decomposition took place, the solution remaining clear.

The β -monobromocinnamic acid, $C_6H_5CBrCHCOOH$.

Wt. taken.	Time of boiling.
0.3015 gram	20 minutes

No decomposition took place, the solution remaining clear.

The above results seem to prove that although the method described by Schulze can be used in certain cases, its application is a limited one.

CHEM. LABORATORY, WORCESTER INSTITUTE OF INDUSTRIAL SCIENCE.

NOTES ON THE HÜBL METHOD FOR THE EXAMINATION OF OILS AND FATS.

BY RUSSELL W. MOORE.

During the past year the analysis of butter and other fats has received much attention in the chemical laboratory at Princeton. The various methods were subjected to rigid tests, and other fats and oils were also examined by the same methods, in order to ascertain whether they could be used to adulterate butter without fear of detection. The result of this extended examination has been a decided verdict in favor of Reichert's process.

The method of Hehner was found to be liable to pronounce as genuine butter, mixtures of butter with cocoanut oil; while that of Köttstorfer is unreliable from the fact that mixtures of oleo-margarine and cocoanut oil were made in such a manner as to come within the prescribed limits.¹

Recently the method of Hübl,² based on the amount of iodine

¹ Chemical News, December 5th, 1884.

² Dingler's Polytechnisches Journal 253:281, and abstracted in American Chemical Journal, November, 1884.

absorbed by oils and fats, has been examined. All oils and fats consist of various proportions of the glycerides of the fatty acids of the acetic, acrylic and tetrolic series. These glycerides are acted upon differently by iodine according to the series to which they belong; the acetic series remaining indifferent, while each molecule of the acrylic unites with two atoms of iodine, and each molecule of the tetrolic series with four.

Although the acids behave thus differently towards iodine, the amount of this element absorbed by any given oil is constant. Thus by treating any oil or fat with an excess of iodine, and, after the lapse of some time, estimating the excess by a standard solution of hyposulphite of sodium, the amount of iodine absorbed can be obtained.

By this process Hübl has examined a large number of oils and fats, and has obtained results varying, from Japanese wax, which absorbs but 4.5 grams of iodine per 100 grams, to linseed oil, which will absorb as high as 160 grams.

The following results were obtained in strict accordance with the directions laid down by the author in the original article. The process was found to be most convenient and expeditious, and the transition point of the final titration is extremely sharp. The author recommends the following amounts to be taken for analysis:

Drying oils,	.2 to .3 gram.
Non-drying oils,	.3 .4 “
Solid fats,	.8 1.0 “

My experience has been that it is best to take the lowest amounts recommended, as an excess of iodine is thus secured.

The following results were obtained by duplicate analyses, and the “iodine figures” or amounts of iodine absorbed by 100 grams of oil for the most part agree closely with those given by Hübl:

Linseed oil,	155.2
Poppy oil,	134.0
Cottonseed oil,	108.7
Rapeseed oil,	103.6
Benne oil,	102.7
Sweet almond oil,	98.1
Mustardseed oil,	96.0
Peanut oil,	87.4
Olive oil,	83.0
Lard (melted in laboratory),	61.9

Palm oil,	50.3
Oleomargarine No. 2,	50.0
" No. 3,	50.0
Butter I,	32.8
" II,	19.5
" III,	38.0
Cocoanut oil,	8.9

The process, while furnishing an excellent means for detecting mixtures of some oils, as, for example, olive oil with cottonseed or benne oils, is of no practical value for the examination of butter for foreign fats; since oleomargarine and lard, the ordinary substitutes for butter, have iodine figures considerably higher than that of butter, while that of cocoanut oil lies much below. Thus a mixture might be made of lard and cocoanut oil or oleomargarine and cocoanut oil which would have the same iodine figure as butter. In proof of this the following mixtures were made and examined:

I. { Lard, 40 per cent. } { Cocoanut oil, 60 }	Iodine figure 32.2
II. { Oleomargarine, 55 per cent. } { Cocoanut oil, 45 }	Iodine figure 35.5
III. { Butter I, 50 per cent. } { Oleomargarine, 27.5 } { Cocoanut oil, 22.5 }	Iodine figure 35.4

The specific gravity of the cocoanut oil used was .9167 at 37.7° C., which is sufficiently high to bring the mixtures above the specific gravity of .911, which is taken to be that of butter.

The amount of iodine absorbed by different butters varies widely. In eight samples Hübl found a maximum figure of 35.1, and a minimum of 26.8. He also observes that when the fat has undergone any serious decomposition the iodine figures will fall much lower. The truth of this remark is seen in Butter II, which was in a very advanced stage of decomposition, and gave figures considerably lower than the lowest obtained by Hübl.

A comparative view of the results of the examination of several samples by the four different methods is here given:

	Hehner.	Köttstorfer.	Hübl.	Reichert.
*Oleomargarine 2,	95.56	197.4	50.0	.6
* " 3,	...	195.0	50.0	.4
*Butter II,	86.01	227.0	19.5	13.25
* " III,	86.49	224.0	38.0	13.1
Mixture III,	89.50	227.5	35.4	8.7

The samples starred were examined by the Hehner, Reichert and Köttstorfer methods by Professor Cornwall, and the results embodied by him in his report to the New Jersey State Board of Health for 1884.

Butter II was examined by these three processes while fresh, but not by the Hübl process until it had undergone serious decomposition.

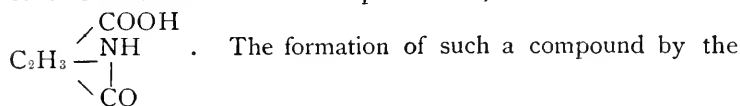
Thus cocoanut oil, as in the case of the Hehner and Köttstorfer methods, would also rob that of Hübl of any practical value in the examination of butters, while the claim of the Reichert process to be the only one to give reliable results remains unimpaired.

JOHN C. GREEN SCHOOL OF SCIENCE,
PRINCETON, N. J., *January 24, 1885.*

ON THE ACTION OF METHYL IODIDE ON ASPARAGINE.

BY ARTHUR MICHAEL AND JOHN F. WING.

In 1879 P. Griess¹ investigated the action of methyl iodide on asparagine, and obtained, beside tetramethylammonium iodide, a new acid, formed from asparagine by the elimination of a molecule of water. This acid was shown to be monobasic, and was considered the lactimide² of aspartic acid, with the constitution



action of methyl iodide on asparagine, seemed to us to be open

¹ Berichte, 1879, 2116.

² Lactimide is generally considered as $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH} \diagup \text{NH} \\ | \quad \diagdown \\ \text{CO} \end{array}$, but there is hardly any doubt that its molecular weight is double that of the above compound, and its constitution is represented by

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH} - \text{NH} - \text{CO} \\ | \\ \text{CO} - \text{NH} - \text{CH} - \text{CH}_3. \end{array}$$

to considerable doubt, and we made the following experiments in the hope of better establishing its constitution.

We can confirm Griess' statement on the preparation of the acid, and have nothing to add to his description of it except that it melts, under decomposition, at 217° . An analysis of the acid melting at that temperature gave the following results:

	Theory for $C_4H_5NO_3$.	Found.
C	41.74	41.76
H	4.35	4.81
N	12.17	11.75

If the constitution proposed by Griess be correct the acid should be reconverted into aspartic acid by treating with strong mineral acids. The substance dissolved in concentrated hydrochloric acid on heating, and, on boiling the solution, a separation of a crystalline substance was noticed. A further amount of the same substance was deposited from the solution on cooling. This compound was purified by crystallisation from water, and was shown to be fumaric acid, by its properties and by the following analysis:

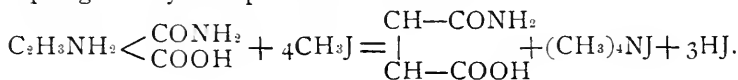
	Theory for $C_2H_2(COOH)_2$.	Found.
C	41.39	41.66
H	3.44	3.72

It is not necessary to use strong acid to convert the so-called asparaginimide into fumaric acid, as boiling it with dilute hydrochloric acid causes the same decomposition, although it is somewhat slower in its action. This decomposition is also effected by heating with alkalis. Boiled for several hours with caustic soda an evolution of ammonia was noticed, and a precipitate of fumaric acid was formed on addition of an acid. The formation of fumaric acid by the action of acids and alkalis shows quite conclusively that the constitution proposed by Griess cannot be correct, for such a substance should give aspartic acid, which we have shown to be stable toward acids at a much higher temperature than employed in the reaction.¹ The following experiment gives further evidence as to the improbability of the constitution suggested by Griess. Aspartic acid was dissolved in caustic potash and methyl alcohol and a weight of methyl iodide added equal to that of the substance taken. The solution was kept alkaline, and methyl

¹ Berichte, 1885, 2984.

iodide added until no further reaction took place. About five times as much methyl iodide was needed as aspartic acid. The solution was heated until the methyl alcohol was expelled, and gave, on addition of an acid, a deposit of fumaric acid.¹ It is evident that if the substance were asparaginimide, that substance should also have been found in this reaction.

The properties of the substance agree perfectly with those of the acid amide of fumaric acid, and the action of methyl iodide on asparagine may be represented as follows:



It still remained an open question whether the compound is not the acid amide of maleic acid, since that acid goes over into fumaric acid on boiling with hydrochloric acid. For the purpose of proving this point, the following experiment was made: Two grams of the amide were dissolved in glacial acetic acid, and an equivalent amount, in proportion of equal molecules, of bromine added. The solution was allowed to stand several days at ordinary temperature, when the bromine had disappeared in greater part and a crystalline substance was deposited. The deposit proved to be unchanged acid fumaramide. The filtrate evaporated on a water-bath left a residue, and was purified by several crystallisations from hot water.

A bromine estimation gave the following result:

0.2546 gram of substance gave 0.3486 gram of AgBr.

Theory for $\text{C}_2\text{H}_2\text{Br}_2 < \begin{array}{c} \text{CONH}_2 \\ \text{COOH}^2. \end{array}$		Found.
Br	58.18	58.26

The dibrom-compound crystallises from water in colorless, rectangular plates that decompose without melting. If the original compound is the acid amide of fumaric acid, the β -dibromsuccinic acid should be obtained by treating it with strong acids, whereas if it is a derivative of maleic acid it should yield the α -dibrom acid. On heating the amide with strong hydrochloric acid it dissolved, and, after heating a short time, deposited small white crystals on cooling. These crystals were purified by crystal-

¹ It seemed possible that this fumaric acid should show optically active properties, as it was formed from aspartic acid at a low temperature. It is, however, without action on polarised light, as is also the acid fumaramide.

lisation and corresponded in their properties; they decomposed on heating to 205° to β -dibromsuccinic acid. This experiment shows that the product of the action of methyl iodide on asparagine is the acid amide of fumaric acid.

The close analogy shown by ethyl iodide in its reactions to those of methyl iodide would have led to the supposition that the acid fumaramide would also be formed in its action on asparagine, but several experiments show that this is not the case. Under the same conditions that methyl iodide acts on asparagine, an alcoholic, alkaline solution of ethyl iodide is entirely without action either on asparagine or aspartic acid. A reaction takes place when an alcoholic, alkaline solution of aspartic acid and ethyl iodide is heated to 100° in a sealed tube, but fumaric acid is not formed in the reaction.

The splitting off of ammonia from aspartic acid by the action of methyl iodide is certainly an unexpected reaction, since that acid is stable under conditions which seem much more favorable for such a decomposition. It is possible, however, that if dimethyl-aspartic acid could be obtained it would be found that it has a less stability, and the elimination of ammonia from aspartic acid is due to the previous formation of the dimethyl derivative; which, under the action of a strong alkali and methyl iodide, is decomposed into dimethylamine and acid fumaramide; the base is then converted into tetramethylammonium iodide by the further action of methyl iodide. It would be of interest to investigate the action of methyl iodide in other amido-acids, such as glutamic acid and tyrosine.

TUFTS COLLEGE, MASS., *Feb.* 1885.

REVIEWS AND REPORTS.

A TREATISE ON THE PRINCIPLES OF CHEMISTRY. By M. M. Pattison Muir, M. A., F. R. S. E., Fellow and Prælector in Chemistry of Gonville and Caius College, Cambridge. Cambridge: at the University Press, 1884.

When one sits down and calmly thinks over the present state of chemistry as illustrated by the way in which most chemists regard the problems of their science, the conviction is easily reached that the methods of investigation now in vogue are far from ideal. The great problem to be solved is, of course, the nature of chemical action. What are the distinctive features of the simplest chemical reaction? What, for example, can we learn in regard to the action of hydrogen upon chlorine? As is well known, the almost universal tendency is to consider the nature of the substances brought together, then to shut the eyes, and, after the action is over, see what has come of it. An enormous amount of valuable information, and, indeed, most of the knowledge of chemical action we possess, has been gathered in this way. And for obvious reasons: the interval between the bringing together of the substances and the formation of new ones is generally so brief that no method of observation will reach it. Though this is not always true, it must be acknowledged that the difficulties in the way of making accurate observations at different stages during the accomplishment of chemical reactions are very great. Hence, most chemists have preferred, and now prefer, to occupy themselves with problems concerning the composition of substances, and it is highly probable that for many years to come most of the work done will be in the same direction. Fortunately, however, there always have been, and there are still, those whose thoughts tend toward that important interval of action which we ordinarily ignore, and slowly facts are discovered which throw light upon it. These facts are described in different journals, and generally without reference to each other, so that it is a difficult matter, for one who does not devote a large amount of time to the task, to coördinate them and see exactly what bearing they have upon the fundamental problems of chemistry.

In the book which forms the subject of this notice the author gives the results of his studies in the field referred to, and also treats of other matters which are of fundamental importance to chemistry regarded as a science. To quote from the preface:

"It (the book) is addressed to students who have already a considerable acquaintance with descriptive chemistry, but it is hoped that by such students the book will be found complete in itself; so that while it certainly deals with chemical principles and

theories on the supposition that its readers have some knowledge of chemical facts, yet the book may fairly claim to rank as a systematic treatise on chemical philosophy. . . .

"The book is divided into two parts. The first part is occupied with the statement and discussion of the atomic and molecular theory, and the applications thereof to such subjects as allotropy, isomerism, and the classification of elements and compounds. Somewhat full accounts are also given, in this part, of thermal, optical, and other departments of physical chemistry, in so far as the results and methods of these branches of the science are applicable to the questions regarding the composition of chemical systems which are connoted by the term Chemical Statics.

"The second part of the book is devoted to the subject of dissociation, chemical change and equilibrium, chemical affinity, and the relations between chemical action and the distribution of the energy of the changing system. These, and cognate questions, I have ventured to summarise in the expression, Chemical Kinetics."

In regard to the first chapter which treats of atoms and molecules, it need only be said that the subject is looked at in much the same way as the majority of chemists look at it at the present day. Instead, however, of stating dogmatically that bodies consist of molecules, and molecules of atoms, the author brings forward the facts, and shows how the prevalent views have been evolved by a consideration of the facts. In regard to the molecular theory he says: "No theory asserting the continuity of matter has been found capable of explaining the observed phenomena of matter; hence, to accept the molecular theory is, at present, the only feasible working hypothesis, is simply to obey the dictates of the scientific method."

Having reached the conclusion that matter consists of molecules, the next step is to investigate these molecules, and to see what evidence can be gained concerning their complexity. The author regards the study of the phenomena included under the head of nascent actions as of importance in this investigation, and hence considers with some degree of fulness the work of Brodie, Gladstone and Tribe, Tommasi and Traube. The work of Traube on the conditions under which hydrogen peroxide is formed, is taken up in detail. The result reached is, that the hypothesis according to which in nascent action we have to deal with the action of atoms furnishes a satisfactory, partial explanation of the phenomena, but that other things must be taken into consideration. In the action of nascent hydrogen, for example, the effects are due, not only to the hydrogen, but also to the other substances present. "Hydrogen, as it is produced by the action of sodium-amalgam, appears to possess properties different from those which characterise hydrogen produced by the action of zinc on dilute sulphuric acid; attempts to explain these apparent differences lead to fresh researches; we become impressed with the conviction that chemistry is not the study of this element or that, regarded as a kind of matter with certain fixed physical proper-

ties, but that processes of change are the subject-matter of the science, and that to explain any one of these we must take into account each and all of the reacting bodies, and each and all of the conditions under which the total change is proceeding."

Next the *dualistic theory* of molecules as introduced into chemistry by Berzelius, and the *unitary theory*, or *theory of types*, which took its place, are considered, and the subject of *equivalency of atoms* is then taken up. The author is largely influenced by Lossen's views in his treatment of this subject. He closely follows Lossen's method in dissecting the prevalent notions in regard to valency, bonds, saturated and unsaturated compounds, and like many others is strongly impressed by the imperfections of these views. He does not, however, for this reason propose to abandon them entirely, but rather he attempts to find out what is of real value in them and to emphasise this. He holds that "from a consideration of solid or liquid compounds only no trustworthy conclusions as to the valencies of the atoms in the molecules of these compounds can be deduced"; and "that it is certainly better—in the present state of knowledge—to apply the theory of valency only to gaseous molecules."

Passing on we find next a section devoted to the subjects of *Allotropy* and *Isomerism*. Inquiring into the causes of the many facts included under these heads the author says: "Granting that variations in the properties (chemical and physical) of molecules accompany variations in the atomic configurations of these molecules, it is conceivable that the latter variations may consist of

"(1) Variations in the relative positions of the atoms.

"(2) Variations in the distances between the atoms, their relative positions being constant."

Among the arguments brought forward against the latter conception is this: "If the second of the two suppositions is correct, then any molecule containing two atoms should be capable of existing in more than one modification; in other words, every diatomic molecule should be capable of showing isomerism. But there is no certainly established instance of isomerism exhibited by any molecule containing less than three atoms; therefore, as the assumption that variations of properties exhibited by compounds having the same composition and same molecular weight are connected with variations in the relative positions of the atoms composing the molecules of these compounds, suffices to explain the vast majority of well-authenticated cases of isomerism among gaseous molecules, we conclude that it is better, at any rate at present, to build the general theory of isomerism on this hypothesis."

The treatment of the connection between the chemical facts and the prevalent views regarding the constitution of compounds is hardly full enough for the purposes of the book; and so many objections are raised to chemical methods of determining constitution that a student who is not far advanced, and who does not

thoroughly understand the methods, would be led to underestimate their value. The author so delights in the unusual that he is apt to magnify what he calls "residual phenomena." It is plain, however, that on the whole he is in accord with the majority of chemists in regard to the subject of constitution, while he justly censures that too prevalent method of dealing with the problem which results in "those ingenious pictorial representations which are sometimes called the structural formulæ of mineral compounds."

Chapter IV is devoted to the "*Application of physical methods to questions of chemical statics.*" Of the physical methods the first considered are the thermal methods. The subject is treated clearly; indeed it would be difficult to find anywhere a more satisfactory statement in regard to the methods and results of thermo-chemistry than we here have included within fifty-odd pages. After showing that the thermal value of even the simplest chemical change is really the sum of various changes, some of which have a positive and others a negative value, and that in most, if not all cases, it is impossible to assign values to each of the simple changes involved, the conclusion is drawn, that until "the distinction," implied in the terms atom and molecule, "is practically recognised in thermal chemistry, we cannot expect any great advances to be made in applying the mass of data already accumulated to questions of chemical actions and reactions."

Regarding the *law of maximum work* the statement is made that it "is simply a crude application of the principle of the degradation of energy; the principle, namely, that energy always tends to run down from a more available to a less available form. Inasmuch as the production of a chemical compound, with evolution of heat, is an instance of such running down of energy, from the form of chemical affinity to that of heat, it follows that the reversal of this process will require expenditure of work. But the *law of maximum work* does not attempt to analyse the expression *chemical affinity*. Under this head Berthelot includes actions and reactions of different kinds. This is at once apparent from the statement in the *Essai*, that the first fundamental principle of thermal chemistry, viz. "The quantity of heat evolved in a reaction measures the sum of the physical and chemical changes which occur in that reaction"—furnishes the measure of chemical affinities.

"Berthelot's work is saturated with the conceptions of the molecular theory; but, by some fatal perverseness, he refuses to apply this theory to chemical phenomena. While recognising the existence of molecules, and building his generalisations on a molecular foundation, he refuses to accept the conception of atom, or rather he hopelessly confuses it with that of equivalent. The molecule is for him a definite and definable portion of matter, the parts of the molecule are only numbers."

This criticism may sound harsh, but it appears to be just. At

all events we shall be glad to hear what the disciples of Berthelot may have to say in reply. We commend this part of the book to the careful attention of those who have blindly "pinned their faith" to investigations in the field of thermo-chemistry. While something has been learned and much more will be learned in regard to the nature of chemical action by a study of thermal phenomena, it must be acknowledged that the results thus far reached are extremely meagre.

Under the head of *Optical Methods*, the well-known investigations of Gladstone and Dale, Landolt, and Brühl, on the specific rotatory powers of chemical compounds, are fully considered. In regard to van't Hoff's hypothesis which assumes the presence of an *asymmetric carbon atom* in every substance which exhibits rotatory power, and supposes the four bonds of this carbon atom to act in definite directions, the author remarks: "We may object to the extremely crystallographic character of the van't Hoff hypothesis, and to the length to which it pushes the vague notion of 'bonds' or 'units of affinity,' for it seems to regard these as capable of definite arrangement in space; but I think the hypothesis is worthy of careful consideration, because it draws attention to the inadequacy of the prevalent conceptions regarding isomerism and molecular structure, and because it bases the explanation it has to give of the connection between such structure and the properties of compounds on essentially dynamical conceptions."

In Book II which treats of CHEMICAL KINETICS the student will find much that has not been considered in other treatises in the English language. The first chapter is devoted to *Dissociation*, the theories of Pfaundler and Horstmann being specially considered. The subject of the second chapter is *Chemical Change*. After a brief reference to the views of Berthollet, Davy and Berzelius on this subject, the author says: "These great chemists were agreed in regarding the object of chemistry to be an explanation of the changes which matter undergoes; they did not think that the ability to give an account of the physical properties of each kind of matter sufficed to make one a chemist. Chemical change was, for them, continuously proceeding, but it might be checked by the action of electrical, or thermal, or other forces. Their fundamental conception is clearly that of an equilibrium resulting from the actions of different forces, the principal of which are chemical, electrical and thermal." The object of the chapter is "to gain a general view of the conditions and the course of chemical actions." The "facts which must some day find their place in a general theory of chemical action . . . may be roughly classified under four heads: (1) contact-actions; (2) predisposing affinity; (3) induction; (4) influence of mass."

Recent researches, more particularly those of Guldberg and Waage, have thrown considerable light on facts included under the fourth head.

The studies on the influence of mass lead to the conception of

chemical equilibrium, "of every chemically stable system as being in a condition of equilibrium, which is the result of the actions of various forces, some of which are what we usually call chemical, and others physical." Pfaundler's hypothesis of chemical equilibrium is considered, and we are then told that though considerable space has been devoted to it, "it is questionable whether hypotheses such as this are of much scientific value. We have no exact knowledge of the forces acting between the parts of molecules; and we know almost nothing of the mechanism whereby the energy absorbed by this or that substance is employed." Then a paragraph is devoted to Horstmann's "thermodynamical theory of dissociation, which is also applicable, in its broad features, to other cases of chemical equilibrium." "But," says the author, "the whole subject of chemical equilibrium has been treated in a masterly manner by Willard Gibbs." A good account of Gibbs' well-known papers which appeared in the *American Journal of Science and Arts* then follows, and the great importance of these papers is pointed out.

One of the most interesting chapters in the book is that in which the subject of *Affinity* is considered. After a reference to the first views concerning affinity it is stated that "when we come to more recent times, it is very difficult to gain a clear conception of the meaning of the term affinity." "Measurements of the quantities of heat evolved or absorbed during definite chemical changes appear to afford the easiest means of measuring gains or losses of energy, and in this way of the comparative magnitudes of the affinities of different substances.

"But before we can hope to gain exact measurements of affinity, we must have a clear conception of what it is we want to measure. Affinity, I think, is usually regarded as an action, or sometimes as the cause of an action, of some kind, which occurs between the atoms of chemical elements, such action resulting in a loss, or gain, of energy to the system of which these atoms are the constituents. Now, it is possible that chemical affinity may be analogous to electrical potential; that as the existence of a difference of electrical potential between two particles implies the possibility of electrical work being done, so the existence of what might perhaps be called chemical potential between two atoms, means the possibility of chemical work being done. If this supposition were adopted, we should look to electrical methods for the means of investigating chemical affinity.

"To sum up, we may regard affinity as essentially connected with interatomic, and perhaps intermolecular, actions; and we may attempt to obtain measurements of different affinities by electrical methods; or we may be content to connect the term affinity with the actions and reactions which occur when two, or more, chemically distinct substances combine to form new substances; and we may seek to deduce measurements of these actions, either from the velocities of the chemical changes, or from

the conditions of equilibrium of the changing systems, or from observations of the changes of the energies of the reacting bodies.

"The more important attempts which have been made to solve the problems of affinity may all, I think, be classed under these headings. Most important work has been done by Guldberg and Waage, and by Ostwald, in framing and applying a theory of affinity founded on measurements of the velocities of chemical changes, and of the conditions under which equilibrium is attained by given systems.

"Berthelot and Thomsen have devoted themselves chiefly to the thermal aspects of the subjects. Helmholtz, following on the older work of Berzelius, Faraday, Joule and Thomson, has recently made some advances in applying electrical methods to these questions."

After reviewing the works of the authors mentioned, it is shown that the nearest approach to measures of affinity is reached in the results of Ostwald, who has determined what he calls "affinity constants." "These affinity constants are true equivalents; they express power of doing definite amounts of chemical work." It is then further pointed out that, though chemical affinity cannot as yet be satisfactorily measured by thermal methods, these methods may, nevertheless, throw light on the differences between the affinities of substances in various analogous reactions. Speaking of the possible applications of electrical methods for determining affinities, the author quotes the remark of Helmholtz, who says: "I think the facts leave no doubt that the very mightiest among the chemical forces are of electrical origin. The atoms cling to their electric charges, and opposite electric charges cling to each other, but I do not suppose that other molecular forces are excluded, working directly from atom to atom." Until we attach a more definite meaning to it than we do at present the author questions whether it is desirable to retain the word affinity.

From the above sketch some idea of the character of Mr. Muir's book may be gained. For the earnest student, however, this should not suffice. The study of the book can only tend to clearer thinking than is common among students of chemistry, and to thinking on subjects which are of fundamental importance, though usually ignored. There can be no question of the fact that the thoughts of leading chemists are tending towards the subjects treated of under the head of Chemical Kinetics, and we may confidently look for the rapid and important developments of these subjects. Those who have made up their minds that the study of constitution is the one thing needful will find before many years that discussions are taking place which they cannot comprehend. Those who have reached or passed middle life may, perhaps, not become painfully aware of their ignorance before they pass away, but surely it is the duty of younger men who have just entered upon their career and who have high ideals, to familiarise themselves with the subjects which are considered in Mr. Muir's book.

The treatment will be found clear and logical, and the book can be cordially recommended to those who will take the trouble to think, and will not condemn simply because the views of an author may not happen to coincide with those to which they are accustomed. It must be said that Mr. Muir is nothing, if not critical, but it cannot be claimed that he indulges to any great extent in hypercriticism. His remarks which seem most severe are evidently prompted by the desire to find the truth, and having found it, he holds it up stripped of the dross with which it is too frequently covered.

I. R.

NOTE IN REGARD TO THE INFLUENCE OF MAGNETISM ON CHEMICAL ACTION.

Some time ago¹ I described an experiment which seemed to prove that chemical action is, under some circumstances, influenced by magnetism. I afterwards found that somewhat similar experiments had been performed by Robert Hunt,² and that after Hunt, Wartmann³ had worked on the subject, and had come to the conclusion that magnetism does not influence chemical action. In 1882, at the Fall meeting of the National Academy of Sciences, I gave an account of later experiments by myself, and stated that the work would be continued. In 1883, in Vol. I, No. 2, of "Science," I published a short paper, in which I called attention to the fact that I was engaged in repeating Hunt's experiments, and I proposed to continue the investigation as long as there seemed promise of obtaining results of value. The work has suffered some interruption since then, but has at no time been given up. The unsatisfactory results reached in repeating Hunt's experiments have interfered with work in new and more profitable directions. Lately I have secured the services of an assistant, and am now pushing the investigation forward as rapidly as the character of the work will permit. We have already obtained some extremely interesting results in depositing various metals upon iron and nickel under the influence of a powerful magnet, and we are now engaged in the study of the action of various acids on metals. We have found that when iron in a magnetic field is treated with nitric acid, certain parts of the iron are protected, while other parts are dissolved with varying degrees of rapidity according to the position with reference to the protected parts. Experiments with hydrochloric acid give similar results, though it appears that the parts protected are not the same as in the case of nitric acid. A full account of the results reached will be published in due time. The object of this notice is merely to call the attention of other workers to the fact that my work on the general subject of "Chemical Action in a Magnetic Field" has not been abandoned, and that through the aid of the Trustees of the Bache Fund

¹ This Journal, 3, 157.

² Philosophical Magazine [3], 28, 1.

³ *Ibid.* [3], 30.

it is now in my power to continue it without interruption. I have no desire nor right to prevent others from working in the same field, but I should be glad to communicate with any one who may contemplate undertaking such work, as unnecessary duplicating may thus be avoided.

IRA REMSEN.

To the Editor AMERICAN CHEMICAL JOURNAL :

Sir :—I notice in No. 4, Vol. 6, an article by A. H. Elliott, on Water Gas Tar. An examination of this tar was commenced about a year since by Mr. G. P. Adamson, of this laboratory, and is now nearing completion. He finds that the tar contains an unusually large amount of water, that it is very rich in naphthalene and anthracene, and is free from phenols and amido compounds. The light oil dissolves completely in sulphuric acid, showing that it is free from paraffins. This tar forms an excellent source of pure naphthalene, as this can easily be obtained perfectly pure. Further results will be offered in due time.

EDWARD HART.

LAFAYETTE COLLEGE, *Nov.* 1884.

OBITUARY NOTES.

HANS HÜBNER, the head of the Chemical Laboratory at Göttingen, died suddenly July 13, 1884. Hübner was born in 1837, in Dresden, and became connected with the University of Göttingen as associate professor in 1870. He was made full professor in 1874, and, after Wöhler's death, he directed the entire work of the laboratory. He contributed very largely to our knowledge of isomerism phenomena in the aromatic series. He was an excellent teacher, and was highly respected by his students.

HERMANN KOLBE, Professor of Chemistry in the University of Leipsic, died November 25, 1884. He was born in the year 1818, at Ellichhausen, near Göttingen. He studied under Wöhler from 1838 to 1842. From 1842 to 1845 he was an assistant of Bunsen, and in 1846 assistant of Lyon Playfair, in London. In 1851 he became professor of Chemistry at Marburg, succeeding Bunsen in this position. Finally, in 1865, he was called to Leipsic to succeed O. B. Kühn. Kolbe has always been an industrious worker, and achieved results of the highest importance. He and Frankland were certainly the first to call attention to the fact that the carbon atom can unite with only a certain fixed number of other atoms, and this prepared the way for the introduction of the conception of valence. Kolbe first pointed out that organic acids are to be regarded as analogous to formic acid, containing radicals in the place of the

hydrogen of this acid; and that the organic acids bear the same relation to carbonic acid that the sulphonic acids bear to sulphuric acid. With the aid of a keen insight into the nature of alcohols, he was enabled to prophesy the discovery of secondary alcohols and to describe their general properties before they were discovered. As evidence of the literary activity of Kolbe may be mentioned the following works: *Ausführliches Lehrbuch der organischen Chemie*, in 3 large volumes; *Kurzes Lehrbuch der anorganischen Chemie*, 1877, 2. Auflage, 1884; *Kurzes Lehrbuch der organischen Chemie*, 1883. For many years past Kolbe has bitterly opposed the methods of modern chemistry. A careful study of his papers will show that the particular feature of modern chemistry which aroused his ire is the tendency to speculate upon an insufficient basis of facts. He did not object to structural formulas, as such, for he himself used them constantly, but he did object to the free use of these formulas by those who do not comprehend them, and to whom they convey no idea regarding the chemical conduct of the substances represented. In some fundamental matters Kolbe differed from the majority of chemists. His ideas regarding the hydrocarbons, for example, were based upon the conception that the four hydrogen atoms of marsh gas are not equivalent.

HENRY WATTS, F.R.S., Editor of *Watts's Dictionary of Chemistry* and of *The Journal of the Chemical Society* of London, died June 30th, 1884. Mr. Watts's labors were almost entirely of a literary character, and in this way he rendered English-speaking chemists the highest services. It appears that his family is left poorly provided for, and an attempt is to be made to secure, through subscriptions from chemists, a sufficient sum to keep them from want. A committee from English chemists have issued a circular from which the following quotation is taken:

"It having become known to some of the friends of the late Mr. Henry Watts, whose death occurred very suddenly on the 30th of last June, that his widow and family are in very straitened circumstances, an informal meeting was held at the Royal Institution on Tuesday, the 11th of this month. Those present resolved to form themselves into a Committee, with power to add to their number, in order to collect a fund for the benefit of Mrs. Watts and those of her children who are not of an age to provide for their own support. Dr. Atkinson consented to act as Secretary, and Dr. Perkin, President of the Chemical Society, as Treasurer.

"Mr. Watts's public labours for the advancement of Chemical Science may be said to have begun with the translation of Gmelin's '*Handbook of Chemistry*,' the admirable English edition of which was prepared and edited for the Cavendish Society by him. This work occupies eighteen large octavo volumes, of which the first appeared in 1849, and the last in 1871. A work scarcely, if at all, inferior to this in magnitude, and one which has perhaps been of

even greater service to English chemists, both scientific and industrial, is Watts's great 'Dictionary of Chemistry,' which appeared from 1863 to 1881, in eight volumes, containing altogether nearly 9700 pages. Mr. Watts also edited and largely added to the second volume of the late Professor Graham's 'Elements of Chemistry,' published in 1858; he prepared several editions of Fowne's well-known 'Manual of Chemistry,' which he almost entirely rewrote and made into virtually a new work; and in conjunction with Mr. Ronalds and Dr. Richardson, he prepared for Messrs. Baillière, an elaborate treatise on Chemical Technology. Up to the time of his death, and for about thirty years previously, Mr. Watts was Editor of the Journal of the Chemical Society, and in this capacity, as well as in that of Librarian to the Chemical Society, he became personally known to and gained the friendship of very many among the Fellows of the Society."

Dr. Elwyn Waller, School of Mines, New York, will receive and forward subscriptions of American chemists.

RECENT PUBLICATIONS RELATING TO CHEMISTRY.

I.—AMERICAN.

- APPLETON, J. H. Chemistry developed by Facts and Principles drawn chiefly from the Non-metals. New York: Phillips and Hunt.
 CLARKE, F. W. The Elements of Chemistry. New York: D. Appleton & Co.
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